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# Development of the

# Diamond windows - Paris-Edingburgh cell (D-PEC)

for ambient and high temperature experiments

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#### Zusammenfassung

In der vorliegenden Arbeit wurde eine Probenkammer mit zwei Diamanten für eine Paris-Edinburgh Presse (D-PEC) konstruiert und modifiziert, um In-situ-Messungen zu ermöglichen. Die Ermittlung des Probendrucks erfolgte unter Berücksichtigung der Floureszenz-Linienverschiebung von Rubin und der Raman-Linienverschiebung von Quarz. Die Kalibrierung des Probendrucks gegen den Öldruck der D-PEC bei Raumtemperatur wurde bis zu einem Druck von 5 GPa durchgeführt. Darüber hinaus wurde eine Probenkammer konstruiert, die mit einem Ofen und zwei Diamantfenstern ausgestattet ist. Diese Kammer ermöglicht Temperaturen bis zu 1000 K. Anhand von Flourszenzmessung von Rubin und Samarium-gedopten Strontium Borat und Ramanmessungen von Quartz wurde die Hochtemperatur-Probenkammer bis zu Drücken von 6 GPa kalibriert. Zudem wurde die Paris-Edinburgh Presse mit zwei Diamantfenster erstmals bei 272 K und 0.15 GPa mit Schwerionen bestrahlt. Dabei wurde Amorphisierung von bestrahlten Quartz und Apatit beobachtet.

#### Abstract

In this thesis, a gasket with two diamond windows was constructed for a Paris-Edinburgh cell (D-PEC) to enable in-situ measurements. The sample pressure was determined by means of the fluorescence peak shift of ruby and the Raman peak shift of quartz. The calibration of the sample pressure against the oil pressure of the D-PEC at ambient temperature was carried out up to a pressure of 5 GPa. In addition, a gasket equipped with an oven and two diamond windows was constructed, allowing to conduct experiments at temperatures up to 1000 K. This HT gasket was calibrated up to pressures of 6 GPa using fluorescence measurements of ruby and samarium-doped strontium borate and Raman measurements of quartz. In addition, the D-PEC was irradiated with swift heavy ions for the first time at 272 K and 0.15 GPa. Amorphization of irradiated quartz and apatite was observed.

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	Table	1:	List	of	Abbreviations
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abbreviation	definition
cBN	cubic boron nitride
CuBe	copper beryllium
DAC	diamond anvil cell
D-PEC	Diamond windows-Paris-Edinburgh cell
LDM	long-distance microscope
GSI	Gesellschaft für Schwerionenforschung, Darmstadt
HP	high pressure
HT	high temperature
ID	inner diameter
L	length
OD	outer diameter
Р	pressure
PTM	pressure transmitting medium
Т	temperature

# I. Introduction

## I.1. Motivation

For more than two decades, the research group of Prof. Dr. Ulrich A. Glasmacher, Thermochronology and Archaeometry from the Institute of Earth Sciences (Ruprecht-Karls University, Heidelberg), has been collaborating with the Materials Research department (Prof. Dr. Reinhard Neumann; Prof. Dr. Christina Trautmann) of the GSI Helmholtzzentrum für Schwerionenforschung (Darmstadt), to combine the analysis of natural minerals under high pressure with swift heavy ion irradiation (M. K. Lang (2004); Glasmacher et al. (2006); Schuster et al. (2009); Weikusat et al. (2011); Dedera (2015)). This interdisciplinary cooperation called "Irradiation of Matter under Extreme Conditions" (Glasmacher (2012)) involved high-pressure investigations (with Diamond anvil– and Paris-Edinburgh cells) at the heavy ion accelerator facility. For large sample volumes (in mm<sup>3</sup>-range) under high pressure, the Paris-Edinburgh cell (PEC) is an ideal instrument. The research was driven by the following questions:

- Is it possible to change matter under extreme conditions with accelerated heavy ions?
- Can we simulate radioactive decay at Earth mantle conditions?
- Do minerals at high pressure and high temperature induce new materials after irradiation with swift heavy ions?

In 2021, Prof. Dr. L. Tajčmanová joined the cooperative research and started her own research program. The research was conducted in close cooperation with Dr. Michael Burchard and Dr. Stefan Klotz.

This thesis, entitled "Diamond windows-Paris-Edinburgh cell (D-PEC) for ambient and high temperature experiments", expands the in-situ analysis capabilities of the hitherto unique large-volume press. The modifications of the PEC with diamond windows enable an unprecedented combination for in-situ measurements of macroscopic sample volume under high pressure and variable temperatures. The adaptations pose two main technical challenges: thermal regulation of the press and the in-situ analysis of the sample chamber. The first technical goal was to construct accessory components for temperature generation and control for the PE cell. The supplementary equipment comprises thermal control based on resistance heating and cooling sleeves or anvils for maintaining the press body at ambient temperature. Moreover, the in-situ analyses were facilitated by the implementation of two diamond windows within the gasket assembly. The innovative gasket with two diamond windows was adapted to be stable over an extended temperature range. These modifications of the high temperature D-PEC (HT-D-PEC) enable macroscopic material to be held under high pressure (<6 GPa), and medium high temperatures (<1000 K). In conjunction with

accelerator facilities, the modified D-PEC can replicate pressure-temperature (P-T) conditions found in the Earth's interior under the natural effects of radioactive decay. Thus, the D-PEC becomes an efficient instrument for the in-situ investigation of various materials under extreme conditions.

The second technical goal of the thesis is the expansion of an optical and spectroscopic system. For the D-PEC, a high-resolution (spatial and spectral) system was built and tested that used optical imaging and various spectroscopic techniques to directly observe the properties of materials under pressure. The optical attachment enables visualization (photo and video recording) of samples, which are magnified with a long-distance microscope (LDM). In this thesis, the HT-D-PEC was attached to the spectroscopic system. This allowed Raman measurements and ruby fluorescence measurements to be taken. The latter are the standard pressure gauge for diamond anvil cells (DAC). The Raman system was optimized for confocal spectroscopic analysis of different layers within the sample chamber.

Furthermore, the application of HT-D-PEC was first time tested on natural samples, such as apatite and quartz, at the heavy ion accelerator. The impact of radiation-induced amorphization on these minerals has been previously investigated (Douillard & Duraud (1996); M. K. Lang (2004); J. Liu et al. (2008); Meawad et al. (2025)).

The overarching objective of this research endeavor is to establish the D-PEC, akin to the DAC for microscopic samples, as a standard high pressure-high temperature (HPHT) instrument for in-situ observations of macroscopic samples. In the following chapters, the Paris-Edinburgh cell with diamond windows is introduced and its application is performed using in-situ and ex-situ experiments on natural macroscopic samples.

# I.2. The importance of in-situ high pressure analysis in Earth and Materials Science

Fundamental research on problems of condensed matter physics under high compression addresses a variety of phenomena such as phase stability, quantum critical phenomena, and the kinetics of phase transitions. The systematic application of pressure leads to significant insights into the properties of matter, especially their electronic properties. With increasing density of solids and liquids, their physical and chemical properties (kinetic, optical, magnetic, stability and others) change noticeably depending on the pressure. In Earth science, HP experimental investigation is one of the most significant scientific fields in the study of the Earth's structure, which is still enigmatic in its composition and evolution and its resulting effects on the surface. At the beginning of the 20th century, Percy Bridgman began a fundamental redesign of the first HP apparatus (a vertical hydraulic piston pushing into a cylinder) to simulate extreme pressures for the first time (10 GPa instead of the then-standard 0.3 GPa). His investigations of natural minerals aimed at deciphering geological and geodynamic processes: structural modifications, phase transitions, and chemical reactions (Bridgman (1949)). With constantly improved devices, HP experiments under variable low and high temperatures have discovered many innovative applications and newly synthesized substances, as well as new states of matter and special mechanical, electrical and magnetic properties (e.g. superhard materials, supercritical fluid phase, superconductivity, etc.) (Wentorf (1957); Bridgman (1964); Hall (1960); Brandt & Ginzburg (1969)).

In the 1950s, the diamond anvil cell, in which two opposing diamonds squeeze a sample between them, became known as the first visually open HP apparatus (W. A. Bassett (2009)). To date, the diamond anvil cell has established itself as the most widely used instrument for in-situ experiments in Earth science, physics, engineering, and materials science. Some of the most common applications include X-ray diffraction (XRD) for atomic characterization of solids, ultraviolet (UV) light for characterization of materials based on molecular electronic transitions, Raman spectroscopy for characterizing materials based on inelastic scattering of photons, infrared (IR) light (as a heat source and for material characterization based on vibrational frequencies of chemical bonds), or simply visible light for sample visualization and optical microscopy (Whatley et al. (1964); Abebe & Walrafen (1979); Jayaraman (1983)). Various optically transparent materials have been used as window materials for HP instruments, for example salts (NaCl, CaF<sub>2</sub>, CsI, etc.), quartz (SiO<sub>2</sub>), sapphire (Al<sub>2</sub>O<sub>3</sub>) and moissanite (SiC) (Bradley & Bradley (1969); J.-a. Xu & Mao (2000); Goncharenko (2004); Iizuka et al. (2012); Klotz (2012)). Diamond is chemically inert, has a high thermal conductivity and a low coefficient of thermal expansion (Rogalin et al. (2018)). With these properties and its widest transmission range for a superhard material, diamond is superior to any other window material used for multispectral applications. However, the diamond anvil cell is typically limited to a tiny sample size (10-300  $\mu$ m). There are several types of modified diamond anvil cells for large samples (Sterer & Silvera (2006); Utsumi et al. (2009); Dubrovinskaia et al. (2012); Boehler et al. (2013)), and modified large volume presses with diamond windows also exist (Lipp et al. (2005), Sengupta et al. (2012)). However, these HP instruments are rare and all limited to a sample volume of 0.02-1.50 mm<sup>3</sup>.

Many different HP apparatuses and corresponding in-situ methods already exist. But it remains problematic to study macroscopic experiments in real time under unaffected conditions, which is a constant incentive for the development of new experimental HP techniques. Therefore, the Paris-Edinburgh cell with diamond windows was developed. The sample chamber of the PEC is much larger (by a factor of 50-200), but reaches lower pressures (by a factor of 5-15) than that of the diamond anvil cell. In general, the selection of phenomena to be studied is determined by the capabilities of the HP instrument, which are characterized by the ranges of working pressures and temperatures and the size of the sample volume (Khvostantsev, Slesarev, et al. (2008)). The ability to obtain macroscopic samples from PE cell experiments is also very beneficial for ex situ characterization. Since a sample in the mm-range offers easy sample preparation and analysis, leading to statistically more accurate mean values in the resulting data. A large sample volume also favors application in various research areas based on the quantitative measurement of macroscopic physical properties.

# II. The historical development of the Paris-Edinburgh cell

Each Paris-Edinburgh cell includes the Paris-Edinburgh press, the load frame, and a set of anvils with a gasket assembly.

# II.1. Paris-Edinburgh press – the load frame

In the 90ies, the large-volume toroid device was further enhanced for neutron diffraction experiments above 12 GPa (Besson, Nelmes, et al. (1992)). R.J. Nelmes (University of Edinburgh, GB), J.M. Besson (Sorbonne Université, Paris, FR) and associated engineers and scientists developed a compact large-volume HP instrument with an axial aperture in the breech (Figure 1). The name of the so-called Paris-Edinburgh cell (PEC) or Paris-Edinburgh press (PEP) derives from the collaboration of the university cities (Besson, Hamel, et al. (1992)). The name Paris-Edinburgh cell refers to the entire instrument, i.e. the set of anvils with gasket assembly and the Paris-Edinburgh press (Klotz (2012)). The PE press,



**Figure 1:** Cross-section of the V-type Paris-Edinburgh press. (1) anvils and gasket assembly, (2) anvil seats and supporting rings, (3) piston, (4) breech, (5) top plate, (6) hydraulic ram, (7) O-ring, (8) tie-rods, (9) retaining nuts and (10) hydraulic oil inlet. Dimensions are in millimeters. Figure from Besson, Nelmes, et al. (1992)

the load frame, is used with various combinations of anvil inserts and ancillary equipment

for structural studies and measurements of virtually all physical properties of materials (i.e. electron transport properties, thermodynamic and elastic properties, viscosity, seismology, ultrasonic interferometry, etc.) (Mueller et al. (2010), and references therein; Philippe et al. (2016)). Due to its aperture and openings, this type of press is mainly applied for inelastic neutron and X-ray scattering and X-ray diffraction (Klotz et al. (2004), and references therein). Since the radially symmetrical load frames have a simple modular structure and are sold by only one company (MG63, Vergongheon, FR), which has strong connections to the group that initiated the program, the pool of Paris-Edinburgh presses is homogeneous and mostly compatible worldwide.

The PE load frame is manufactured in two different versions: the older V-series (Figure 1) with four columns and the newer VX-series (Figure 2) with two columns (Besson, Nelmes, et al. (1992); Besson & Nelmes (1995); Stishov & Sadkov (2002); Klotz et al. (2004)). Both load frame series with an axial aperture in the breech are available in different sizes (piston diameter 80-150 mm), weights (16-100 kg) and load capacities (50-500 tons) (see Appendix Fig. 71) (Klotz et al. (2004); Klotz (2012)). Thus, pressures of 10-20 GPa can be generated, corresponding to forces of 0.5-5.0 MN (Klotz (2012)). The VX type frame contains two openings, each 140° horizontal and  $60^{\circ}(\pm 30^{\circ})$  vertical, originally integrated for powder diffraction at neutron sources (Figure 2). However, both openings are vertically limited by the inclination of the inserted anvils. These openings are not only important for precise data acquisition for structure determination from the neutron sources, but also for an easy mounting of the gasket assembly. In general, the PE press is a simple squeezer, i.e. the sample volume is uniaxially compressed along the height axis (loading axis) by means of a hydraulic ram. The inner structure of the press consists of two opposed cylindrical pistons, with which the pressure is exerted on the sample chamber. The upper part of the press comprises a breech (1) with a screw closure, which is threaded into the top of the press body (2) (Figure 2). Manually unscrewing the breech allows the attached upper anvil and support plate to be quickly and easily removed and to gain access to the gasket assembly.

The PE VX press design has a peculiar shape of its cylinder (Figure 2) (Patent Nr. 924010747; Klotz et al. (2004)). Under load, radial deformations are limited to less than the height of the O-ring seal, which prevents leaks and jamming of the piston. Such "auto-compensation" is realized by supporting the lower circumference of the hydraulic ram, which is the case for the VX version by separating the piston and cylinder from the press body (Klotz et al. (2004)). This results in high-pressure efficiency compared to other HP devices, while maintaining large sample volumes (approx. 100 mm<sup>3</sup> up to 10 GPa or less than 35 mm<sup>3</sup> up to 25 GPa), depending on set of anvils (Klotz et al. (1995); Klotz (2012)).



**Figure 2:** Cross section (left) and side view of the VX2 PE press (mass 60 kg, capacity 200 t). (1) Breech, (2) body, (3) O-ring seal, (4) piston, (5) cylinder and (6) hydraulic fluid inlet. The azimuthal and equatorial apertures are 60°(as shown) and 140°, respectively. Figure from Klotz et al. (2004).

### II.2. Single-toroidal anvil and gasket assembly

The Paris-Edinburgh cell exists with different sets of anvils such as multi-anvil insert, shear unit, etc. (Le Godec et al. (2005); Bromiley et al. (2009); Fang et al. (2010); Dobson et al. (2005)). I used a type of single-toroidal anvils, which has its roots in the opposed cup anvil. For synthesis of superhard materials (especially diamond), in the Soviet Union (at Institute for High Pressure Physics, Moscow, RU), the large "opposed cupped anvil"-type apparatus was invented (Bradley & Bradley (1969)). This concave hollowed Bridgman anvil, based on the principles of a compressed seal, was further developed into a so-called toroid device for generation of HP (Khvostantsev et al. (1977)). The toroid device is described as comprising two identical coaxial anvils, each of which has at least one circular groove (filled with a solid medium) located concentrically on the mutually facing surfaces of the anvils (Khvostantsev et al. (2004), and references therein). A key distinguishing feature of this single-toroidal anvil from other types of anvils is its toroidal recess for the gasket around the central part of the working surface, resulting in high-pressure generation efficiency (Khvostantsev et al. (1977)). The support of the gasket material, created by enclosing the sample and the central part of the anvil, aims to reduce the deformation of the anvils and the extrusion of the gasket material (Khvostantsev et al. (1997)). In the center, the opposing cups (spherical or conical shape) enclose the sample and the pressure transmitting medium (PTM) (together up to 100 mm<sup>3</sup> in volume) (Khvostantsev et al. (2004)). In the literature, terminology is not consistent and a variety of terms are used, e.g. "cup", "center hole", "dimple" etc.; all these terms describe the entire cavity in the center of the anvil for the sample and the pressure

cell. The values of the maximum pressure achieved in a toroid cell depend on the diameter and material of the anvil (up to 14 GPa for 10 mm anvil diameter and up to 25 GPa with sintered diamond anvils) (Khvostantsev, Slesarev, et al. (2008); Klotz et al. (1995)). The opposed single-toroidal anvils made of hard alloy (mostly cubic boron nitride (cBN), tungsten carbide (WC), sintered diamond) are radially supported by a set of steel rings (Figure 3, 6). The 1.5°inclination of the lateral surface area of the anvil facilitates its pressing into the steel supporting ring with matching cone. By providing support for hoop stress, the 819AW maraging ring reduces the risk of damage to the anvil during pressure generation. The anvils allow a free radiation access of 360°in the horizontal plane, since the toroidal device was mainly developed for the synthesis of macroscopic samples and experiments with neutrons (Besson, Hamel, et al. (1992); Khvostantsev et al. (2004)). In the vertical plane, the anvils are inclined by 7°. Furthermore, even at maximum pressure, the gap between the anvils remains sufficiently large (1-3 mm) to insert thermocouples (Khvostantsev et al. (1997)).



**Figure 3:** Scheme of single-toroidal anvils and gasket assembly. (1) Sample chamber (pressure transmitting medium), (2) pressure cell (inner gasket), (3) spacer (middle gasket) (4) confining gasket, (5) hard-alloy anvil and (6) steel supporting ring. (not to scale)

For these single-toroidal anvils, there are various combinations of different gasket and pressure transmitting materials, depending on the experimental requirements. The gasket assembly must be prepared again for each experiment, as it is a disposable item. It represents the most important component, as it ensures a homogeneous compression of the sample. Requirements for the used materials are inertness (even at high temperatures) and no phase transitions or polymorphism up to at least 10 GPa to ensure (pseudo-)hydrostatic conditions. In addition, low compressibility is important to avoid excessive volume changes. The solids used should have a low shear strength, which depends only slightly on the pressure. Liquids should have a high melting pressure but a low melting temperature (Klotz (2012)). The gasket assembly consists of the confining gasket (4), spacer (3), pressure cell (also called toroid cell for single-toroidal anvils) (2) and sample chamber (1) (Figure 3).

The confining gasket, usually made of a ductile metal (e.g. titanium zirconium, copper beryllium (CuBe), etc.), assures a plastic deformation and a homogeneous pressure distribution inside the sample chamber. The compressibility of a metal gasket is small, but high enough to resist the pressure build-up (Klotz (2012)). It reduces the extrusion of the pressure transmitting material. In addition, the gasket reduces the magnitude of shear stress in the anvils, thus increasing their maximum achievable pressure and extending their service life. Compression and outflow of the gasket in the toroidal recess during pressure rise and release occur uniformly (hydrostatic pressures up to 10 GPa) (Khvostantsev et al. (2004); Khvostantsev, Slesarev, et al. (2008) and references therein).

The pressure cell should be a malleable solid, which is easily compressible under pressure so that it deforms slowly and uniformly. Some authors refer to the pressure cell also as gasket (Klotz (2012)). Hereinafter, it is referred to as the inner gasket. To maintain the pressure built up in the sample chamber for several hours, the inner gasket must not be brittle. The inner gasket can be mineral, metallic or plastic, usually pyrophyllite, talc, salts, lead or boron epoxy are used (Klotz (2012)).

The pressure transmitting medium is the sample chamber or can be the sample itself. The shape and internal friction of the gasket assembly (confining gasket, inner gasket and PTM) create hydrostatic or at least pseudo-hydrostatic compression of the sample volume, which is favorable for single crystals as samples (Khvostantsev et al. (2004); Müller et al. (2006)). When a sample is immersed in a liquid or gaseous PTM, it hydrostatically transfers the applied force to the sample contained within. Since the results obtained under hydrostatic conditions are intrinsic material properties, i.e. not dependent on system size or the amount of material in the system, such as temperature, density, refractive index, etc., the collected data can be compared with validated literature values. As it is the kinematically most restricted state (in stable equilibrium), all frictional and inertial stresses vanish in a fluid at rest. Distilled water, a mixture of ethanol-methanol (4:1), glycol and Fluorinert are often used as PTM (Klotz (2012)).

# II.3. Ion-PEC with one conical diamond window

In Heidelberg, the Paris-Edinburgh press VX4 has been modified for the use of irradiation with accelerated heavy ions of matter under pressure (Glasmacher (2012)). In order to expand the experimental possibilities, in 2008 Prof. Glasmacher acquired two identical VX4 Paris-Edinburgh presses, which were equipped with the standard single-toroidal anvils made of cubic boron nitride (cBN) (Ø: 20 mm) (Klotz (2012)). The modification comprised a channel in the backing plate and the inner die of the backing seat behind the anvil, through which the ion beam is guided close to the anvils (Figure 4, 5 and 6) (Glasmacher (2012)). The status quo of the Ion-PEC with a gasket including one conical diamond window was developed by Dr. Michael Burchard (Burchard et al. (2009)). At the ram side, this modified VX4 type press has a second channel through the cylinder and piston, which allows further neutron beam access (Figure 4, 9). This axial channel at the top and at the bottom of the press body, virtually predestines the load frame for the insertion of open anvils (section 3.1).



**Figure 4:** a) Photo and b) half section of the modified VX4 Paris-Edinburgh cell. (1) Press body, (2) cylinder, (3) piston, (4) breech, (5) backing plates, (6) steel binding rings, (7) centering rings (sleeves), (8) anvils, (9) lower channel and (10) upper channel. Black bar indicates 5 cm.

The used VX4 press, compressing samples typically 1.0-40.0 mm<sup>3</sup> in volume (depending on gasket assembly), is relatively lightweight (60 kg) and easy to transport (Ø: 230 mm, L: 290 mm) despite its considerable capacities (maximal 200 tn) (Klotz (2012)).

# II.4. Gasket assemblies with one diamond window

Dr. Michael Burchard developed the gasket assembly for ion irradiation and carried out the first swift heavy ion irradiation experiments at GSI (Burchard et al. (2009); Weikusat et al. (2009); Burchard et al. (2012)). In Cave A at SIS18 (GSI), the first feasibility test of the Ion-PEC was performed with a gasket assembly made of copper beryllium and silver. To avoid strong ion-induced activation of the material, an inner gasket made of pure silver was introduced due to its ease of fabrication, low cost and inertness to ion irradiation (Burchard et al. (2009)). To avoid chemical reactions inside the sample chamber, it was filled with silicone paste as pressure transmitting medium. The samples, zircon ( $Zr[SiO_4]$ ) crystals embedded in the silicone paste, were pressurized to ca. 6 GPa at ambient temperature. The <sup>132</sup>Xe ion irradiation was performed with an initial energy of 300 MeV/u and a fluence of

 $1.5 \times 10^{12}$  ions/cm<sup>2</sup> (Burchard et al. (2009)). The deactivation time until the Ion-PEC could be handled was around 5 months mainly due to tungsten carbide components behind the single-toroidal anvils.

In order to replace the expensive copper beryllium alloy, which is usually used as a gasket material, various types of steel such as tool steel, stainless steel and structural steel (mat. No. 1.1620, 1.4305 and 1.7225) were successfully tested (Weikusat et al. (2009)). The first ion irradiation with a steel-silver gasket assembly was performed under the same conditions (applied fluences and pressure as mentioned above). The samples were a mixture of annealed zircon and rutile ( $TiO_2$ ) crystals of several mm in size (Weikusat et al. (2009)). Both crystal phases were chosen because of their well-documented ion-induced radiation damage, which can be easily detected by Raman spectroscopy. Comparison of Raman spectra of the irradiated and pristine zircons from the same batch revealed a significant decrease of band intensity, an increase of the bandwidth and a shift of the band centers to lower wavenumbers after irradiation. All effects are a clear indication of radiation damage (Weikusat et al. (2009); and references therein).

The first-time insertion of one diamond was possible by the replacement of the upper anvil with a cBN anvil with a hole in it, an axial channel along the loading axis (also called an optical channel). In the center of the open anvil, above the channel, is a cup for a conical diamond window. Although the diamond transmits pressure to the sample chamber, it primarily functions as an optical window (hence referred to as diamond window hereinafter). This conical diamond in the upper anvil provides access for swift heavy ion beam. In 2012, the first irradiation test with one conical diamond window was performed in Cave A using a focused U-ion beam with an initial energy of 250 MeV/u (Burchard et al. (2012)). A calcite crystal (CaCO<sub>3</sub>), suitable due to its well-defined Raman bands, was embedded in salt powder (NaCl) as PTM and confined by a CuBe gasket. Raman spectra of calcite recorded through the diamond window of the PE cell at ambient and under pressure enabled pressure determination via Raman shift. The 2.1 cm<sup>-1</sup> shift of the  $\nu_1$  band (1085 cm<sup>-1</sup>) indicates a pressurization of 0.9 GPa. Most of the activation disappeared two days after the irradiation. After two weeks, the Ion-PEC could be handled safely (Burchard et al. (2012)).

# III. Methods

### III.1. Diamond windows-Paris-Edinburgh cell

The diamond windows-Paris-Edinburgh cell (D-PEC) is a VX4 type Paris-Edinburgh press containing open single-toroidal anvils with two diamond windows and the corresponding gasket assembly (Figure 4 - 6). When the D-PEC is connected to the hydraulic pump and other attached equipment (e.g., spectroscopy set up, heating set up, etc.), the whole assembly is called the D-PEC system. The portable device is primarily designed for performing in-situ experiments on large-volume samples at heavy ion irradiation facilities. The axial channel ending in the two diamonds serves for irradiation with swift heavy ions and as access for optical and spectroscopic analysis. In this thesis, the channel is applied as an optical access to the sample chamber, for measuring fluorescence and Raman signals and for swift heavy ion irradiation. The diamonds act as windows, not pressure intensifiers as in the DAC.

The press is anchored in transport frames made of aluminum strut profile in order to turn it sideways or to transport it easily. Acrylic glass was integrated into the strut profile to prevent material from being thrown around if the anvil fails during an experiment. The new adaptations of the anvils for inserting two diamonds and the modifications for a high temperature gasket are described below.

To generate pressure, a commercial oil pump (P2232, Enerpac, Menomonee Falls, USA) is mounted on the hydraulic inlet at the bottom of the press body. The hydraulic pump generates oil pressures measured on a digital pressure sensor (P105 and alpha-c, FGP Instruments, Weymouth, UK). By injecting hydraulic fluid (HF-95 Hydraulic Oil, Enerpac) to the cylinder, the lower piston lifts and pushes against the fixed upper one. A check valve (Sitec, Maur, CH) secures the oil pump from the press.

#### III.1.1. Single-toroidal anvils with two one-sided spherical diamond windows

The single-toroidal anvil with an axial channel is made of K10 tungsten carbide (Hawedia, Marklkofen). The maximum pressure achieved corresponds to about 12 GPa for this Ø 25 cm tungsten carbide anvil. The anvil is beveled 7°in the horizontal plane. In order to access the sample chamber optically and spectroscopically, the press body requires anvils that leave space for Raman fibers and/or laser diodes from both sides. The new axially open anvils were inserted into the upper and lower pistons. The axial channel (Ø: 1.4-5.0 mm) in the center of the anvil narrows toward the side of the sample chamber (Figure 5). With an exit opening of 1.4 mm diameter at the sample chamber and 1.0 mm length, the cylindrical aperture becomes conical and has a cone angle of 27°. For diamond anvil cells, there is a distinct minimum anvil tension at an aperture angle of 25-30°, implying that optimum anvil performance can be obtained with an aperture viewing angle that is ideal for spectroscopic or

diffraction work (Adams et al. (1993)). The anvil design has a toroidal recess for the gasket, a 2 mm deep groove with 13 mm diameter. In the center of the anvil, a funnel-shaped recess with a diameter of 6 mm was designed for the inner gasket. Above the open channel is a hemispherical indentation of the same size as the new designed diamond window (Figure 5). For a perfect fit, the spherical cavity of the single-toroidal anvil was polished with diamond paste prior to the first experiment. This results in beneficial surface hardening, better sealing properties and easier alignment of the spherical diamond in its seat than without polishing. The diamond is inserted and its spherical pavilion is glued to the anvil.



**Figure 5:** a) Drawing and c) half section of the open single-toroidal anvil made of tungsten carbide. b) Half section of the one-sided spherical diamond. Black bar indicates 1 mm.

The specially developed anvils contain new one-sided spherical diamonds with girdle diameter of 2.84 mm (Scimed GmbH, Isselburg). The CVD (chemical vapor deposition) diamond was ordered in optical grade, the most optically transparent quality, i.e. nitrogen concentrations in the lower <50 ppm range (Detlef Hüffer, owner of Scimed, priv. communication). A special feature of the spherical diamond is that all facets are rounded; the girdle, the crown, the pavilion and the culet have a circular shape. In addition, the culet size and girdle facet are extremely large (categorized by GIA cut grading system for standard round brilliant diamonds), as a thin girdle can increase the risk of damage such as chipping (Lanzl et al. (2006)). The culet size is not only a few 100 microns (like in diamond anvil cells), but is almost 2 mm and faces towards the axial channel, while the table (facing towards the inside of the sample chamber) measures 1.4 mm. In the diamond anvil cell the large area reduction (80%) of the table face to the culet face causes high pressures to be developed within the

sample (>100 GPa) (McMillan (2003)). In the D-PEC, the diamonds with their extremely large culet size act primarily as windows. Compared to the conical diamond, the resolution of in-situ observation with spherical diamonds is improved, as they act like a solid immersion lens (enlargement of  $\sim$ 2.4X of the image) (Dubrovinsky et al. (2017)).

In the process of development of a high temperature gasket, conical diamonds replaced the one-sided spherical diamonds. This conical diamond had a culet size of 1.2 mm and a table size of 1.3 mm (Type Ia - SOP25894, Böhler-Almax design 30°; Almax easyLab, Diksmuide, BE). The advantage of type I diamonds is the low absorption of short-wave X-rays and the transmission of UV, visible to far-infrared radiation.

#### III.1.2. Steel-silver gasket

The gasket assembly for ambient temperature was slightly modified in the manufacturing process due to the insertion of two diamonds. After reevaluating different steel types, structural alloyed carbon steel proved to be the most beneficial in terms of processing and cost efficiency (compared to that in section II.4.). The steel gasket (Mat.No. 1.7218) was manufactured by the in-house precision mechanics workshop (at the Institute of Earth Sciences, Heidelberg) with a CNC precision lathe. A silver rod (99.99% silver,  $\emptyset$  6.2 mm, Goodfellow, Hamburg) was cut to a length of 6 mm. To prepare the inner gasket, the silver cylinder and the steel gasket were placed on the lower anvil with one spherical diamond inserted. So the outer and inner gasket were pre-compressed up to approximately 2 kbar for 2 minutes. The precompression merged the inner gasket and confining gasket, and the negative shape of the anvils was transferred to the gasket. At the center, where the imprint of the diamond is visible, the sample chamber was drilled directly into the silver with a carbide drill bit (Ø: 2.5 mm) (see Appendix Fig. 72). The actual sample chamber is a cylindrical space, the drill hole, squeezed between the two diamonds (Figure 6). To remove excess silver and chips, manual grinding and smoothing of the outer edges and surfaces of the drilled hole were necessary. The prepared gasket was again placed on the lower tungsten carbide anvil without moving the diamond. To press the diamond in the silver gasket, the pressure of the D-PEC is increased to approx. 4.0-5.5 kbar. After merging the lower diamond with the silver gasket, the sample chamber can be filled with a liquid or solid PTM and the sample of interest. In Figure 6, the pre-compressed gasket is drawn visually floating. For optimal light transmission, the diamond culets should be arranged parallel to each other.

The initial volume for the sample and the PTM is about 25 mm<sup>3</sup>, which decreased to around 12 mm<sup>3</sup> after pressure generation (depending on the maximum pressure applied and the kind of PTM).



**Figure 6:** a) Exploded view and b) photo of open single-toroidal anvils and steel-silver gasket after the experiment. (1) Open tungsten carbide anvil, (2) one-sided spherical diamond, (3) steel gasket, (4) silver inner gasket, (5) sample chamber (water) and (6) sample. Black bar indicates 1 mm.

# III.2. Spectroscopic systems

In the process of the development, the D-PEC was tested with different spectroscopic systems at Heidelberg University and at GSI.

#### III.2.1. The long-distance microscope

The long-distance microscope (LDM) was selected as magnifying tool due to its ease of use and compactness (small and lightweight). The K2 LDM (L.O.T-Oriel, Darmstadt) has the greatest range of focus in the industry and controls spherical aberration. This magnifying device is modular. The LDM consists of interchangeable objectives, the basic unit of the K2 microscope are two TR-lens tubes, the modules T-58, T-19, M-46 with a 10x ocular, T-36, UNIPAR 1 and 2, as well as a C-Mount for attaching an optical fiber (Figure 7, 2). Depending on the lenses selected, the long-distance microscope consists of twelve or ten lenses. The basic unit works with internal focusing (Figure 7, 3), i.e. it can focus without changing the working distance. A confocal magnification of the sample is necessary to focus along the entire length of the sample chamber, approximately 4 mm (depending on the pressure applied). In addition to the focus ring for magnification, the LDM has a built-in iris diaphragm to control depth of field and light attenuation, allowing easy adjustment of contrast and resolution (Figure 7, 4). The used configuration in conjunction with the CF-2 objective achieves a working distance of 180 mm and a magnification of 190x (see Appendix table 7). The LDM mounted on a workstation is interposed for all subsequent optical and spectroscopic recordings and analysis. For visual imaging experiments, the sample chamber was illuminated with a diode inserted into the rear channel (ram side) of the D-PEC. To

ensure good alignment of the sample chamber and the LDM, the D-PEC was adjusted with respect to the beam of a diode attached to the rear end of the axial channel (see Figure 73).



**Figure 7:** Photo of the long-distance microscope with attached moving stages. (1) C-mount for camera, (2) mount for spectrometer cable, (3) internal focusing, (4) iris diaphragm, (5) y stage, (6)  $\times$  stage and (7) z stage.

#### III.2.2. Raman probe

The Raman setup consisted of the long-distance microscope placed in front of the Raman probe. The SuperHead (Horiba Jobin Yvon, Bensheim), a high efficiency Raman sensor, transmits the excitation laser source and receives the reflected signal via two optical waveguides. The glass fiber cables (400  $\mu$ m, Ocean Optics) transmit and receive from 200-4000 cm<sup>-1</sup>. The SuperHead provides a good confocal depth resolution, which allows multiple layers to be distinguished and interfering substrates to be ignored. Piezo-controlled focusing ensures optimal signal levels. High efficiency filters incorporated within this special Raman sensor provide effective laser and Raman filtering (Figure 8). The SuperHead was attached to an adjustable table in order to ensure the positioning of the laser beam. The laser beam

was focused on the sample in the D-PEC through the SuperHead and the long-distance microscope.



Figure 8: Optical layout of the beam path inside the SuperHead.

# III.3. Materials

#### III.3.1. Water

For the phase transition experiment of water, the steel-silver gasket was filled with about 0.025 ml distilled water as hydrostatic pressure transmitting medium and the sample itself. For the swift heavy ion irradiation experiment, distilled water was filled in the sample chamber as hydrostatic pressure transmitting medium. The water was cryogenically loaded with nitrogen.

#### III.3.2. Ruby

The most prevalent pressure gauge for optical open gaskets, especially for diamond anvil cells, is the ruby  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>, a red corundum doped with chromium (Forman et al. (1972)). In the following experiments, synthetic ruby was used.

#### III.3.3. Quartz

Quartz (SiO<sub>2</sub>) is the most prevalent mineral in the Earth's crust with an almost pure composition. The peak shift of the Raman signal of quartz has been studied intensively (Schmidt &

Ziemann (2000); and references therein). The peak shift intensively depends on pressure and temperature and not on chemical variations (Li et al. (2025); and references therein).

#### III.3.4. Samarium-doped strontium borate

The compound  $SrB_4O_7:Sm^{2+}$  was chosen as pressure sensor, as it has major advantages compared to ruby. Especially at high temperature the samarium-doped strontium borate presents a negligibly small temperature-induced wavelength shift (Datchi et al. (1997)). My samples of  $SrB_4O_7:Sm^{2+}$  were prepared by Dr. F. Datchi, consisting of a fine powder (grain size about 1  $\mu$ m) of strontium borate doped with 5 mol% of divalent samarium (Datchi et al. (1997); and references therein).

#### III.3.5. Apatite

For the swift heavy ion irradiation, an apatite (Durango, MX) was used. Its ion-induced amorphization has been studied previously (J. Liu et al. (2008); Weikusat et al. (2011)). The irradiation of the two apatites was conducted at a perpendicular angle to their c-axis. Before irradiation, the apatite crystals were annealed at 673 K for 1 h (Green et al. (1986)).

# IV. The Diamond windows-Paris-Edinburgh cell for in-situ large-volume experiments at ambient temperature

The axial channel, passing through the whole D-PEC body, was tested as optical and spectroscopic pathway. Initial optical observation experiments were conducted with the steel-silver gasket.

# IV.1. Optical observation

Experiments carried out in the D-PEC can be combined with all optical and spectroscopic methods as applied for the diamond anvil cell. The aim of this technical subsection is, on the one hand, to visually observe the processes inside the sample chamber (via photos and video recording). On the other hand, analytical methods (Raman and fluorescence spectroscopy) are tested in-situ. Raman and optical spectroscopy are versatile tools for nondestructive characterization of a wide range of properties of novel materials and minerals in-situ at extreme and ambient conditions. The axial channel passing through the entire body of the D-PEC is tested for the first time as an optical and spectroscopic pathway. Initial experiments (section IV.2.) were performed with the steel-silver gasket. Further experimental setup descriptions of these preliminary results are documented in Dörr (2018). In the following, various devices, setups, different types of instruments are tested and combined.

#### IV.1.1. Chromatic aberration

An inherent problem of the diamond in combination with the LDM (and generally any lens system) was the chromatic aberration. Since transverse (lateral) chromatic aberration did not occur in the center of the image, but only increases towards the edge, it is negligible for imaging of the sample chamber of D-PEC. This aberration happened primarily at the edges of the circular image of the sample chamber, i.e. where the press channel can be seen. Axial (longitudinal) aberration occurred when different wavelengths of light were focused at different distances from the lens (focus shift), which was typical along the focal length. To investigate this at the LDM, a cold light source (KL150, Schott, Mainz) was connected in front of a Czerny-Turner monochromator (HRS2, Jobin Yvon, Bensheim) for illumination (Figure 9). The monochromator can be adjusted to an accuracy of 1 nm, with an error of approx.  $\pm 3$  nm. Measuring a focus curve with the monochromator, the LDM indicated a 2 mm shift of the focus point between 425 nm and 650 nm. When testing different lens systems for focusing inside the sample chamber, the focus point shifted by 10 mm (Dörr (2018)). Severe

longitudinal aberration can be reduced by decreasing the aperture (diaphragm) of the LDM and shutter speed (or higher ISO values) of the camera, which increases depth of field.



**Figure 9:** Scheme of the optical observation system with monochromator to observe chromatic aberration. (1) Camera, (2) LDM, (3) D-PEC, (4) monochromator, (5) cold light source, and (6) Mac.

A diamond was placed in the sample chamber. This diamond was doped with boron at a depth of 300 nm and in a circular shape (see Appendix Fig. 74). This doping has sharp edges, making it easy to focus. 10 focus curves were recorded with the diamond and an average was determined. The focus curve is shown in figure 10.



Figure 10: Diagram of the mean value of the chromatic aberration of the long-distance microscope.

# IV.2. Feasibility tests and calibration of the D-PEC with a steel-silver gasket assembly

#### IV.2.1. Introduction

In the fields of Materials and Earth science, there is an essential need to understand the behavior of both synthetic and natural materials. This knowledge is crucial not only for advancing technological innovations but also for addressing environmental challenges. By unraveling how these materials behave and interact with their surroundings, scientists can develop more sustainable solutions and enhance our understanding of the planet's processes. This research typically involves conducting experiments, which serve as the primary method for investigating material properties.

To gain insights into the kinetic, optical, and magnetic properties of matter, visually and spectroscopically transparent devices are necessary. The diamond anvil cell is the most commonly used in-situ device for observing and measuring materials under high pressure. The DAC enables a broad spectrum of pressures, reaching up to 460 GPa (Dubrovinskaia et al. (2016)), though it typically operates between 100-200 GPa. Such pressures even exceed those found within the Earth's interior. Diamonds are transparent to a wide range of radiation, including X-rays, ultraviolet and infrared light. Therefore, the DAC enables in-situ measurements of samples using various techniques, such as fluorescence, Raman, optical absorption, photoluminescence, Mössbauer, X-ray spectroscopy, and Brillouin scattering (e.g. Holzapfel (1996); W. Bassett et al. (1996); Iota et al. (1999); M. Lang et al. (2015)). The "optically open" design also allows its use on accelerators. The DAC has become the primary tool for high pressure and crystallographic studies at synchrotron (light) sources as well as at ion beam accelerators combined with spectroscopic methods (Klotz (2012); M. Lang et al. (2020)).

The Paris-Edinburgh cell (PEC) is another uniaxial press commonly used at accelerator facilities due to its one centrally located channel and wide openings on the horizontal plane, established for neutron scattering in the 0-10 GPa range on spallation sources (Besson, Nelmes, et al. (1992)). Due to its channel and openings, this type of press is mainly applied for inelastic neutron and X-ray scattering and diffraction (Klotz et al. (2004); Mezouar et al. (2005); Bull et al. (2009)). Typically, applications are magnetic structure determination and analysis of lattice and spin dynamics, particularly in materials with a low Z-number, which are highly sensitive to high pressure-induced volume changes (Klotz (2012)). The Paris-Edinburgh press frame is used with various combinations of anvil inserts (Dobson et al. (2005); Le Godec et al. (2005); Bromiley et al. (2009); Fang et al. (2010); Millar (2011); Klotz (2012); Hunt et al. (2014); Philippe et al. (2016)). In contrast to the DAC (sample size 10-300  $\mu$ m), the sample chamber of the PEC is much larger (by a factor of 50-200), but reaches lower pressures (by a factor of 5-15). In the past, the PEC was frequently provided as an additional option to the DAC for beamline setups, as a macroscopic alternative and

for ultrasonic measurements and energy dispersive X-ray diffraction (Fei & Wang (2000); Decremps et al. (n.d.); Di Cicco et al. (2006); Evans et al. (2006)). Unlike the transparent DAC, which supports optical investigations, the non-transparent PEC is limited to only a few analytical techniques and excludes those needing optical access.

At Heidelberg University, we modified the Paris-Edinburgh press by adding a new axial channel and by installing new anvil inserts with an axial channel (Glasmacher (2012)). This axial channel passing through the entire body of the ion-PEC was built for an ion irradiation at large-scale and high-performance facilities (Weikusat et al. (2009)). A corresponding metallic gasket with one conical diamond window was developed for this ion-PEC (Burchard et al. (2012)). This gasket assembly was preliminary tested for heavy ion irradiation on natural minerals at the GSI (Gesellschaft für Schwerionenforschung/Heavy Ion research facility) in Darmstadt. The ion-PEC was further modified and used for the first time to allow optical and spectroscopic access from both sides of the sample chamber. Here, I present the first functional open single-toroidal anvil with two diamond windows and a steel-silver gasket assembly, designed for ambient temperature use (Figure 11). Such a newly designed Diamond windows-Paris-Edinburgh Cell (D-PEC) can achieve extreme conditions for in-situ investigation of the optical and spectroscopic properties of macroscopic materials. In particular, the D-PEC is capable of compressing millimeter-sized samples up to 10 GPa, equivalent to the conditions found in the Earth's lithospheric mantle and asthenosphere. The D-PEC, incorporating the two diamonds, is as versatile as the DAC and can be combined with all optical and spectroscopic methods and used at any type of accelerator, including heavy ion beam accelerators. This broadens the scope for conducting in-situ experiments on minerals. In the future, the D-PEC with its steel-silver gasket assembly can be accessible to any user, as it is straightforward to implement and simple to maintain.

The initial feasibility test involved observing a phase transition in-situ, specifically the transformation of water into ice. Water, known to be naturally hydrostatic, has been extensively studied, with many in-situ observations and Raman studies of water to ice crystallization in DACs (Cross et al. (1937); Lee et al. (2006)). The water to ice VI transition occurs at 0.98 GPa at ambient temperature (10000 kg/cm<sup>2</sup> at 299 K; Bridgman (1913)). For small samples (0.08–0.13 mm), water freezes into ice VI at 0.9 GPa with minimal pressure overshoot, remaining stable up to 2.1 GPa before transitioning to ice VII at ambient temperature with a significant pressure drop (Chen & Yoo (2011)).

Furthermore, calibrating this new gasket assembly is needed to ensure that the HP device delivers accurate and consistent results as the pressure increases. Therefore, here, I provide the cross calibration as a first experimental approximation to measure the "true" pressure inside the sample chamber of the D-PEC. The present in-situ HP experiments were targeted up to 5 GPa at ambient temperature. A calibration using spectroscopic sensors is the most accurate method for detecting delayed reactions or excluding ex situ deformation. The aim was to establish a correlation between the oil pressure applied by the hand pump, which moves the piston and the pressure exerted on the sample volume. As pressure-transmitting

medium (PTM) filled in the sample chamber, a mixture of methanol and ethanol (4:1) was chosen. This mixture has no phase transition and is commonly used in the DAC community due to its hydrostatic properties up to 9.8 GPa (Angel et al. (2007)).

The standard method for in-situ spectroscopy and pressure monitoring in DACs is the ruby fluorescence, which is defined up to 0.55 TPa (J. Xu et al. (1986)). A small fragment of synthetic ruby ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>) is implemented in the sample chamber, and then excited with a laser (Syassen (2008)). Since the first ruby fluorescence measurements by Forman, Piermarini and colleagues in 1972, numerous scientists have made contributions to establishing a precise ruby pressure scale under diverse experimental conditions. Therefore, to calculate pressure from the peak shift, there are formulas with different estimates for the variables (Mao et al. (1986); Dewaele et al. (2004)). Here, I used the IPPS-Ruby2020 standard, which is most commonly suggested by the DAC community to unify the interpretation of fluorescence shift of ruby (G. Shen et al. (2020)).

To obtain more accurate results and to validate the fluorescence measurements, a Ramanactive pressure gauge was chosen. For this, quartz was chosen as a representative phase due to its fundamental importance in crustal processes. Furthermore, it is a well-studied mineral in its vibrational spectroscopy due to its common use as a barometer (elastic thermobarometry) in Earth Sciences. Temperature and pressure variations in Raman spectra of quartz have been studied intensely (Raman & Nedungadi (1940); L.-G. Liu & Mernagh (1992)). Schmidt and Ziemann (2000) reviewed data and developed a new formula for calculating the shift in vibration mode frequency as a function of pressure and temperature. By measuring the peak shift of the Raman signal of quartz, the pressure exerted on the mineral can be calculated. Until now, this type of calibration has been carried out using Raman spectroscopy up to 2.1 GPa with a  $\mu$ m-sized quartz ( $\emptyset$ : 0.3 mm; 0.04 mm thickness; Schmidt & Ziemann (2000)). Here, I extend this calibration to 5 GPa.

Comparing fluorescence and Raman signals is an ideal method for calibrating and determining precision of the D-PEC. These pressure gauges could thus provide consistent and repeatable results for experiments and may be used as a standard material in the future.

#### IV.2.2. Methods

#### IV.2.2.1. Experimental and spectroscopic setup

The Paris-Edinburgh press VX4 with diamond windows was used in combination with an optical and two spectroscopic setups. All measurements were conducted in the backscatter configuration, with the exception of optical imaging. The videos were recorded with the sample illuminated from the opposite side of the camera. The three setups consisted of the spectroscopic components mounted behind the channel of the D-PEC and its gasket assembly.



**Figure 11:** a) Schematic structure and b) photo of D-PEC connected to the optical observation setup. c) Photo of steel-silver gasket assembly. d) Half section of the D-PEC. e) Half section of the open single-toroidal anvils and steel-silver gasket assembly with two diamond windows for ambient temperature application. (1) Cold light source (KL 150, Schott), (2) D-PEC, (3) steel-silver gasket assembly, (4) long-distance microscope, (5) camera (Coolpix 4500, Nikon), (6) Mac computer with video grabber, (7) one-sided spherical diamond, (8) steel gasket, (9) silver gasket and (10) water sample. The green arrow shows direction of video recording. The yellow arrow shows direction of illumination with light source.

#### IV.2.2.1.1. Experimental procedure

The gasket assembly was mounted on the tungsten carbide anvils ( $\emptyset$ : 25 mm), while the D-PEC is positioned vertically. The gasket for ambient temperature was made of a silver double cone ( $\emptyset$ : 9.8 mm) and a steel toroid ( $\emptyset$ : 15 mm). The annealed silver was pressed with the prepressing jig with 100bar/tn and then centrally drilled ( $\emptyset$ : 2.5 mm, 6 mm length). The sample chamber was sealed at both ends by one-sided spherical diamonds. With about 50 bar/tn the diamond mounting jig imprinted the lower diamond (facing away from Raman signal) into the silver.

In case of the phase transition experiments, the steel-silver gasket assemblies were filled with distilled water as pressure transmitting medium and the sample itself. Pressure was applied using a hydraulic oil pump (P2232, Enerpac) with a digital pressure gauge. For this kind of experiments, the pressure values were estimated with the following formula:

$$P_{cal}[GPa] = 0.005976 * P_{oil}[bar]$$
(1)

For example, an oil pressure displayed 200 bar corresponds to an assumed pressure of 1.2 GPa (12 kbar) in the sample chamber. However, as it is unclear how well the pressure transfer of the pressure medium to the sample chamber occurs, it can be assumed that the pressure shown here is in reality lower. The pressure was increased slowly until first crystallization started. Further experimental setup descriptions of these preliminary results (experiment 10) are documented in M. Dörr (2018), master student whom I supervised.

For the calibration series, a mixture of methanol and ethanol (4:1) was inserted as the PTM in the drilled silver gasket. The pressure gauge was a small fragment of synthetic ruby  $(\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>, 1 mm, irregular fragment). A fragment of single-crystal quartz (0.5x0.5X2.0 mm; Valmalenco, IT) was inserted with its c-axis oriented along the Raman signal. After sealing the sample chamber with a closing pressure of 20 bar, the entire D-PEC was positioned horizontally to align it with the spectroscopic setup. The oil pressure was increased in 15 bar/steps. Pressure release was measured in about 100 bar/steps.

#### IV.2.2.1.2. Optical imaging and spectroscopic setup

#### Optical imaging and Raman setup at Heidelberg

The optical observation system comprised a cold light source (KL 150, Schott), the longdistance microscope (LDM), and a camera were connected to a Mac computer for recording (Figure 11). To sufficiently illuminate the sample chamber for video recording, the gooseneck light guide was inserted into the lower axial channel of the channel of the D-PEC. A Nikon Coolpix 4500 camera (4.0 MP) was mounted on the C-mount of the LDM. The camera settings were exposure value +2.0, ISO 800 and aperture f2.7. The camera was connected to a Mac computer via an USB video grabber module (Ezcap-172 USB 2.0 Video Grabber, Top-Longer) including a video editing software (ArcSoft ShowBiz 3.5). It is important that the long-distance microscope, camera and D-PEC are adjusted in parallel for each experiment, so that the sample is in focus.

The Raman setup consisted of the long-distance microscope placed in front of the Raman probe (SuperHead, Horiba). The LDM was employed with different objectives (CF3 and CF2), resulting in a maximum focal length of 130 mm and 220 mm. The spectrometer (iHR 320, Horiba; f/4.1, 1200 g/mm and 1800 g/mm, CCD camera 1024x256 pixel) was connected via an optical fiber with metallic shielding (Ocean Optics;  $\emptyset = 100 \ \mu\text{m}$ , L =1 m). The Raman spectra of water were obtained at different ranges (between 200 and 3700 cm<sup>-1</sup>) and integration times (50 to 200 s). I used a 532 nm laser (Ventus 532, Laser Quantum; 90 mW, Noise/Power Stability: <0.15% RMS) for exciting Raman signals. Calibration of the spectrometer was accomplished using a Hg lamp, resulting in an accuracy of at least  $\pm 1 \ \text{cm}^{-1}$ .

#### Fluorescence and Raman setup at GSI

The spectroscopic setup for fluorescence and Raman measurements consisted of the longdistance microscope screwed to the Raman probe (Vishead, Horiba; f = 40 mm) with a customized adapter (Figure 12). The Raman probe was connected to the spectrometer (iHR 320, Horiba; f/4.1, 1800 g/mm, CCD camera 1024x256 pixel) via an optical fiber with metallic shielding (Ocean Optics;  $\emptyset = 100$  m, L = 10 m). The spectrometer was calibrated using a green laser and a Si-Wafer. The accuracy was at least  $\pm 1$  cm<sup>-1</sup>. The green laser (Sapphire, Coherent; 532 nm, used 10-25 % of 100 mW, Noise/Power Stability: <0.8% RMS) excited the fluorescence and Raman signals. This spectroscopic setup, the spectrometer, the Raman probe and the laser were used in the Raman laboratory at GSI in Darmstadt.



**Figure 12:** a) Photo of the D-PEC aligned with spectroscopic setup. b) Steel-silver gasket assembly with two diamond windows. (1) Optical fiber, (2) Raman probe (VisHead, Horiba), (3) long-distance microscope, (4) multi-axis stage, (5) Diamond-windows Paris-Edinburgh-Cell, (6) laser shadow casted through sample chamber on wall, (7) one-sided spherical diamond, (8) steel, (9) silver, (10) ruby, and (10) quartz immersed in methanol-ethanol mixture.

In this series of experiments, the LDM was used with the objective lens CF2 (but without the spacer), resulting in a focal length of 220 mm. During pressure changes, refocusing of the working distance was necessary to obtain a strong Raman signal. For each set oil pressure, the fluorescence signal of the ruby was measured in the range of 680-710 nm with an integration time of 1 s. The Raman spectra of quartz were measured in the range of 100-1200 cm<sup>-1</sup> for 300 s.

#### IV.2.2.2. Data processing

The spectra were analyzed using a Python script for quartz (Groß (2023)). Additionally, I modified the quartz script for fitting the ruby double peaks and calculating the sample pressure from their peak shift. Both scripts used lmfit to search for the highest measured intensities in the given range (Newville et al. (2016)). The Python scripts subtracted a linear background from the raw data and fitted the peaks using the pseudovoigt model. The pseudovoigt function is a probability distribution combining two profiles, the Gaussian and Lorentz, to fit analyzing data from spectroscopy or diffraction (Temme (2010)). For the ruby data the double peaks at 694 nm and 692 nm were fitted in the range 690-702 nm. The quartz peak at 464  $\text{cm}^{-1}$  was fitted in the range 420-560  $\text{cm}^{-1}$ . The scripts read the .txt-files of the measured data. The data input consisted of two columns: The first column contained the wavelength or wavenumber and corresponding intensities in the second column. After fitting the data points, the intensity was plotted against the wavelength (nm) (, and wavenumbers (cm<sup>-1</sup>) respectively), illustrated in figure 13. The number of sigma values of 1, 2, or 3 give probabilities of 0.6827, 0.9545, and 0.9973, respectively (Newville et al. (2016)). Consequently, the array of  $2\sigma$  residues in a.u., representing the difference between the model and the data (Figure 13, blue dots), was covered within a 95% confidence interval. The deviation of measured to fitted data, displayed as  $2\sigma$  residues, was hardly recognizable and was generally below 10% (see Appendix Fig. 75). The pressure calculation was based on the values obtained from this fitting procedure. The pressure calculation scripts used the spectra at 0 bar as the reference points. For ruby and quartz, the peak shift was calculated using a polynomial form of the second order to fit the nonlinear behavior. In case of ruby, the double peaks R1 and R2 peaks were fitted, 694 nm and 692 nm respectively. The pressure was calculated using the formula

$$P[GPa] = 1.87(\pm 0.01) * 10^3 * \frac{\Delta\lambda}{\lambda_0} * [1 + 5.63(\pm 0.03) * \frac{\Delta\lambda}{\lambda_0}]$$
(2)

after the IPPS-Ruby2020 standard (G. Shen et al. (2020)). The errors associated with the calculated pressure values for ruby were determined through propagation of uncertainty and were found to be below  $\pm 0.09$  GPa. The measured R1 peak positions, at 694 nm, were inserted as  $\lambda$ -values. The last measurement at 0 bar oil pressure with R1 at 694.19 nm was

used as  $\lambda_0$  value. The initial measurement at 20 bar exhibited the same peak position.  $\Delta\lambda$  is the difference between the  $\lambda_0$  and measured ( $\lambda_x$ ) value at a certain pressure.



**Figure 13:** a) The spectrum of ruby at 505 bar was measured for 1s twice. b) The spectrum of quartz at 505 bar was measured for 300 s twice. Both measurements are taken with 1800 g/mm. The black dots represent the measured data points, while the red dashed line represents the fitted spectrum. The 2 sigma ( $\sigma$ ) uncertainty band is barely visible. The deviation of the measured from the fitted data is displayed as  $2\sigma$  residues in blue below.

For quartz, the pressure was calculated using the formula

$$P[MPa] = 0.36079 * \Delta v^2 + 110.86 * \Delta v \tag{3}$$

,where  $\Delta v$  is the difference between the reference ( $v_0$ ) and current peak position ( $v_x$ ) of the 464 cm<sup>-1</sup> peak (Schmidt & Ziemann (2000)). For quartz, the 464.34 cm<sup>-1</sup> peak, measured at 0 bar oil pressure, was fitted as reference. The pressure derived from the quartz peak shift has an error of ±50 MPa (Schmidt & Ziemann (2000)).

The fitted peak positions of ruby and quartz with calculated pressure values are shown in table 8-11. Regression analysis was used to calculate the trend line of the calculated pressure for ruby and quartz.

#### IV.2.3. Results

The first experiments were the optical observation of the phase transition of water to ice, documented via photos and video recording. This was followed by Raman measurements. After that, the pressure in the D-PEC sample chamber was calibrated via the application of ruby fluorescence and Raman measurements.

#### IV.2.3.1. Water to ice phase transition

#### IV.2.3.1.1. Optical in-situ observation of water under pressure

The initial phase of the study involved the collection of in-situ video recordings and photographs of the interior of the sample chamber during the water to ice phase transition. The visual observation of a sample through the diamond windows and long-distance microscope connected to a camera was tested during a two-day experiment.

Figure 14 illustrates the pressure build-up within 14 minutes in photographic sequence, extracted from a video recorded by the long-distance microscope with the CF2 objective. The room temperature was 298 K. The maximum pressure of approximately 12 kbar (1.2 GPa) was estimated from the display of the hydraulic pump, which showed 200 bar. The first images were taken around 2 kbar estimated in the sample chamber (oil pressure of 35 bar) (Figure 14, image 1-3). Image 2 and image 3 show the change of focus (2-4 mm) with the LDM from the front end to the rear end (facing the light source) of the sample chamber. A bigger air bubble (around 0.5 mm) was visible in the rear end. During a pressure increase up to 3 kbar (oil pressure of 50 bar), the image sequence, numbered 1-5, shows the shrinkage of the air bubbles over 4 minutes. The black line visible in all images (see red marking in Figure 14, image 6) is an impurity from the sample preparation, presumably a silver residue. During the first 10 minutes, the pressure in the sample chamber was increased up to 9 kbar (oil pressure of 150 bar). The pressure in the sample chamber raised to the critical point, when the image briefly turned black (Figure 14, image 7). From this point onwards, the pressure was not further increased. A crystallization front formed on the sample chamber wall and built the first larger crystals of ice (Figure 14, image 10). The images 7-8 indicate the onset of the crystallization process. Subsequently the crystals then increased in size to approx. 0.1-0.2 mm (Figure 14, image 12-16). As a consequence of the "healing" of the crystals and the reduction in the number of refractive surfaces, the image became significantly brighter towards the end of the video.



**Figure 14:** The photograph sequence illustrates the pressure build-up (at 298 K). Images 1-6 depict the dissolution of air bubbles and the shift of the focal plane. Images 7-16 illustrate the crystallization of ice. Red circle: a silver particle. The green and red bars indicate the shift of the focal plane from the front to the rear of the sample chamber. The recording time is displayed under each image.

Without changing the pressure, a time-lapse (1 image every 30 seconds) was recorded overnight with the CF3 objective mounted on the long-distance microscope. All of the videos and photos were taken with the same setup of the LDM. This image sequence demonstrates the 'healing' of some crystals and crystal boundaries (see red circle in figure 15). The crystallization resulted in darkening the sample chamber (see red arrow in figure 15).


Figure 15: The growth of ice crystals in the sample chamber was observed at a gradually increasing pressure (at 298 K) (see red circle).

On the following day, an attempt was made to heat the sample chamber with a hot air dryer in order to melt the sample without increasing pressure. The external heating attempted a rudimentary proof of equilibrium melting of ice. Figure 16 shows the use of the hot air dryer on the left side of the gasket assembly. During the first 10 minutes, the ice on the left-hand side began to melt. This process involved the dissolution of grain boundaries, which permitted the influx of more light (Figure 16, image 5). The images show a clear reduction in the crystalline content of the sample (Figure 16, image 3-6). The chromatic aberration of the long-distance microscope is clearly visible in the image on the right side, appearing as rainbow colored.



**Figure 16:** Images of the melting process when the sample chamber is heated with a hot air dryer. The "melting front" can be seen in images 5 and 6.

After removing the heat source, the water recrystallized quickly during 12 s (Figure 17). First, the crystals formed with rounded crystal edges towards the water, and then these

crystallized into smaller crystals with more edges.



Figure 17: The recrystallization of ice (at 298 K).

Based on the visual observation of the phase transition and freezing of water to ice VI (at equilibrium pressure and ambient temperature), the pressure in the sample chamber at the crystallization point was defined at 0.96 GPa (Chen & Yoo (2011)).

#### IV.2.3.1.2. Raman measurements of water

The phase transition experiment was recreated days after the recordings described in the previous chapter because the Raman laboratory is not always available. Raman scattering was used to characterize pressurized samples and to distinguish phase transitions. The setup of the spectroscopic analysis system is similar to that of the optical observation system. The camera and cold light were removed and replaced by a laser and spectrometer. For in-situ Raman measurements, the Raman laser, SuperHead, LDM and spectrometer were adjusted in parallel to the axial channel of the D-PEC to ensure the best signal intensity. Since the focal length is large (due to the length of the press body) and the channel and sample chamber are in the beam path, achieving high signal strength and good signal-to-noise ratio are main challenges in Raman measurements with the D-PEC. Due to the high background (especially for large wavelength ranges) and high intensity loss of the receiving laser beam, the acquisition time was set to up to 200 seconds. The measured Raman spectrum displays the characteristic Raman bands for diamond window, silver (gasket), gases of the air gap (O<sub>2</sub>, N<sub>2</sub>) and water (Figure 18 and table 2). The measured Raman spectra are mostly preliminary and additional Raman measurements are necessary to confirm it. The broadened band at 1000 cm<sup>-1</sup> is probably an interference between the tungsten carbide anvil and the water spectra (after Cross et al. (1937); Pawbake et al. (2016)).



Figure 18: Overview Raman spectrum of inside the sample chamber with 1200 g/mm and 200 s.

Table 2: Materials and associated Raman bands measured in-situ with the D-PEC.

material	Raman band $[cm^{-1}]$	source
water (@RP/RT)	3500	Scherer et al., 1974
ice (@1Gpa/RT)	3250	Lee et al., 2006
diamond	350	http://rruff.info/diamond/display=default/R050206, 27.10.2018
silver	200 and 400	http://rruff.info/silver/display=default/R070463, 27.10.18
0 <sub>2</sub>	1550	Siemann & Ellendorff, 2001
$N_2$	2330	Siemann & Ellendorff, 2001
tungsten carbide	1000	Pawbake et al., 2016

For the following measurements, the bandwidth was reduced and measured twice for 50 s each to eliminate spikes and maximize the resolution of the spectra. The grating was 1200 g/mm. The gasket assembly was heated from the outside with a hot air blower to force the ice crystals to dissolve. Raman spectra of crystallized ice and melting water were recorded. The strongest and most distinct Raman bands of water are the 3230 and 3440 cm<sup>-1</sup> lines. Figure 19 shows Raman spectra of water in range of 3000-3700 cm<sup>-1</sup>, once at 180 bar and after releasing pressure at near atmospheric pressure (8 bar). Three phases of  $H_2O$  are visible: 1/ water at elevated pressure, 2/ after heating under pressure, and 3/ ice

(Figure 19). The spectra were recorded while the applied pressure was just high enough that the water was not yet crystallized (visibly observed). After the pressure was released, the double water peak shifted about 77 cm<sup>-1</sup> to higher wavenumbers (Figure 19). The Raman spectra show the pressure-induced shift of the H<sub>2</sub>O band from 3247 cm<sup>-1</sup> (water before crystallization) to 3324 cm<sup>-1</sup> (8 bar).



**Figure 19:** a) Raman spectra at 8 bar (black) and ca. 180 bar (blue) (measured twice for 200 s with 600 g/mm) b) Raman spectra of water under pressure and ice (measured twice for 200 s with 1800 g/mm). Vertical lines: dominant Raman bands of water.

#### IV.2.3.2. Calibration of the D-PEC at ambient temperature

For each increase and decrease of oil pressure, a fluorescence measurement of the ruby and a Raman measurement of the quartz were performed.

#### IV.2.3.2.1. Ruby results

The measured pressure of the oil pump (in bar) is aligned with the calculated pressure (in GPa) assumed inside the sample chamber (Figure 20). The ambient and current peak positions were used to calculate the pressure inside the sample chamber. As the oil pressure increases, the calculated pressure increases almost linearly. The resulting trend line formula is

$$P_{\rm Rb}[{\rm GPa}] = 6.772 * 10^{-3} * P_{\rm oil} + 0.1748$$
(4)

and agrees very well with the measured data with  $R^2$ -value = 0.9945. The trend line for the peak shift is

$$\lambda_{\rm Rb}[\rm nm] = 2.474 * 10^{-3} * P_{\rm oil} + 7.065 * 10^{-2}$$
(5)

with  $R^2$ -value = 0.9947 (Figure 20). Up to 1 GPa, the calculated pressure is initially slightly lower and then slightly higher than expected from the trend line. A slightly lower pressure ratio is also documented between 160 and 190 bar and at 280 bar oil pressure (gray panels). At 700 bar, the maximum calculated pressure is 5.14 GPa, with corresponding trend line value of 4.9 GPa (-3%).



**Figure 20:** Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the ruby peak at 694 nm (at 298 K) (G. Shen et al. (2020). Filled points represent the increasing pressure, unfilled symbols represent decreasing pressure path. Trend line is  $P[GPa] = 6.772 * 10^{-3} * P_{oil} + 0.1748$  with  $R^2 = 0.9945$ . The gray panels define the regions of interruptions that are described in more detail in the main text.

The oil pressure-releasing path exhibits a parabolic descent, with data points shifted towards calculated pressures compared to the trajectory of increasing pressure. From the highest data point, the calculated pressure drops enormously, by about 0.72 GPa. Between 597 bar and 568 bar, the assumed pressure for ruby decreases by only 0.08 GPa (from 4.42 GPa to 4.34 GPa), approaching values close to the pressure points observed in the ascending path (590 bar with 4.20 GPa). Furthermore, there is a slight increase in the calculated pressure at 529 bar with 4.75 GPa and below 463 bar at 4.31 GPa the assumed pressure for the ruby shows a parabolic drop.

#### IV.2.3.2.2. Quartz results

The Raman signal intensities of quartz were generally lower, mostly less than half as strong as the ruby fluorescence signals (Figure 13). The calculated pressure for the quartz peak shift against the measured oil pressure is aligned (Figure 21). The trend line is

$$P_{Oz}[GPa] = 6.353 * 10^{-3} * P_{oil} + 0.2771$$
(6)

with  $R^2$ -value = 0.9936. The trend line for the peak shift is

$$v_{Oz}[GPa] = 5.017 * 10^{-2} * P_{oil} + 3.367$$
(7)

with  $R^2$ -value = 0.9930. Above 1 GPa the calculated pressure increases almost linearly with increasing oil pressure. The similar outliers to that of ruby occur again between 175 bar and 190 bar (gray panels). In addition, from the first to the second measurement at 280 bar, the pressure drops from 2.10 GPa to 1.92 GPa (-9%). The maximum calculated pressure at 700 bar is 4.41 GPa, while the trend line indicates a value of 4.77 GPa (+8%).



**Figure 21:** Diagram of the measured oil pressure (in bar) against the calculated pressure (in GPa) after the peak shift of the quartz peak at 464 cm<sup>-1</sup> (at 298 K) (Schmidt & Ziemann (2000)). Filled points indicate increasing pressure and unfilled symbols indicate decreasing pressure. Trend line is  $P[GPa] = 6.353 * 10^{-3} * P_{oil} + 0.2771$  with  $R^2 = 0.9936$ . The gray panels define the regions of interruptions that are described in more detail in the main text.

The decrease in calculated pressure derived from quartz peak shift is also parabolic. The

calculated pressure only drops to 4.27 GPa and 4.22 GPa on the way from the highest oil pressure to 597 bar and 568 bar respectively. Subsequently, at 529 bar, the calculated pressure assumed for quartz increases to 4.33 GPa, before following its parabolic trend.

#### IV.2.3.2.3. Comparison of ruby and quartz

The comparison of the calculated pressure of ruby and quartz in Figure 22 shows almost a perfect linearity between 1-4 GPa. After the D-PEC was sealed, initial measurements at 30 bar show that the calculated pressure for ruby is 0.11 GPa, while for quartz it is 36% lower at 0.07 GPa. At an oil pressure of 160 bar, the ruby had a calculated pressure of 1.24 GPa and the quartz had 1.17 GPa, resulting in a deviation of only 6%. As the pressure increases above 1.2 GPa, the calculated deviation from the linear trend is less than 5%. Above 1.8 GPa, the calculated pressure is slightly higher for ruby values. This effect becomes more pronounced above 2.5 GPa. At higher pressures, the calculated pressure for ruby and quartz deviates by less than 5%, except at 5 GPa. Ruby has a calculated pressure of 5.14 GPa at 700 bar, while quartz has a calculated pressure of 4.41 GPa. The calculated pressure for ruby is 1.06 GPa higher than that for quartz (+20%).



**Figure 22:** Diagram of the calculated pressure of ruby against the calculated pressure of quartz peak in GPa (at 298 K). Trend line is  $P_{Rb}=P_{Qz}$  with  $R^2 = 0.9040$ . Filled points represent increasing pressure path and unfilled symbols the decreasing of pressure path.

The pressure calculated for the decreasing pressure path (unfilled markers) is slightly higher than that for the increasing pressure path (Figure 22). The initial pressure release measurement at 597 bar yielded a calculated pressure of 4.42 GPa for ruby and 4.27 GPa for quartz. These values are 4% higher than the calculated pressure for the sample chamber along the pressure increasing path. The oil pressure dropped from 568 to 529 bar, causing an increase in the calculated pressure for ruby from 4.34 GPa to 4.75 GPa and for quartz from 4.23 to 4.33 GPa. For the last measurement at 0 bar, the calculated pressure for ruby was 0 GPa.

#### IV.2.4. Discussion

#### IV.2.4.1. Water to ice phase transition

#### IV.2.4.1.1. Optical observation

The effectiveness of visually observing a sample through diamond windows using a longdistance microscope was tested over a two-day experiment. The pressure within the sample chamber reaches the critical point, resulting in a brief blackout of the image. The phase transition from water to ice was recorded. The transition was indicated by the darkening of the optical image. The following schematic drawing illustrates the presumed effects of Ostwald ripening on the illumination through the ice crystals (Figure 23). When the image of the camera briefly turned black, the sample chamber was probably filled with crystal nuclei. No light could penetrate the sample chamber because there were so many crystal nuclei that the light was absorbed by refraction (Figure 23a). As the experiment progressed, Ostwald ripening caused these nuclei to grow into larger crystals. This growth reduced the number of smaller nuclei, allowing more light to pass through the sample chamber as the larger ice crystals caused less light refraction (Figure 23b). After illumination comes back, first grain boundaries of the ice crystals started to be visible (Figure 14, image 8).



**Figure 23:** Schematic drawing of the influence of Ostwald ripening on the illumination through the crystals. Yellow: light, black circles: crystal nuclei.

In these phase transition experiments, it is likely that ice VI crystallized (see Figure 24). At ambient temperature (at 298 K), ice VI forms at a pressure of approx. 1 GPa (Chen & Yoo (2011)). It is unlikely that Ice VII formed during the experiments, carried out up to 200 bar displayed on the hydraulic pump, as this phase of ice only forms above 2.3 GPa corresponding to 380 bar oil pressure. The assumed pressure path of these water to ice VI transition is displayed in figure 24.



**Figure 24:** The P-T diagram of  $H_2O$  is shown with a red line, along which the experiments in this study proceeded (at 298 K). Figure from Chen & Yoo (2011)

An experiment conducted in a DAC demonstrated that metastable ice VII can be formed

through a rapid pressure increase of 0.16 GPa per second (Lee et al., 2006). A clear distinction can be observed in the morphological characteristics of the two ice phases, as they exhibit different crystal structures. Ice VII (cubic) crystallized needle-shaped, while ice VI (tetragonal) formed irregularly clumpy (Figure 25 after Lee et al. (2006)). There is a striking resemblance of ice VI (Figure 25, image c) to images of ice that have been generated in this study (Figure 14-17).



Figure 25: Comparison of a) water, b) ice VI and c) ice VII. Figure from Lee et al. (2006)

When heated rapidly, the ice melts unevenly due to uneven heat distribution. In this experiment, the melting process starts from the left side, where the hot air dryer was placed at the gasket. The melting front extended along the sample chamber (Figure 16).

#### IV.2.4.1.2. Raman measurements of water and ice

The Raman measurements presented here are only preliminary and were initially conducted without a pressure gauge using the Raman setup (Section IV.2.2.1.2.). Consequently, the following discussion is speculative and further measurements are needed to ascertain the pressure within the sample chamber. Additionally, contamination from adhesive, residues from cleaning tools, air, or the long-distance microscope itself can introduce additional peaks, broadening the Raman spectra. For the Raman measurements water and ice, the measurements were compared to the Raman peak frequency of ice VI as a function of pressure between about 9 and 21 kbar at 294 K (according to Abebe & Walrafen (1979)). For ice VI, a temperature increase of 1 K triggers a shift of +0.12 cm<sup>-1</sup> and a pressure increase of 1 kbar (0.1 GPa) causes a shift of -7.2 cm<sup>-1</sup>. The pressure also increased due to thermal expansion. Since three parameters (pressure, temperature, and phase transition) affect the water, the shift in band position to higher Raman bands was expectable.

Assuming that the Raman bands of ice VI (according to Abebe & Walrafen (1979)) are also reasonable for water, these pressure values were calculated from a band position at

P [GPa]	Raman band $[cm^{-1}]$	Error [cm <sup>-1</sup> ]
0.05	3324	0.0
0.10	3320	0.1
0.20	3313	0.3
0.30	3306	0.5
0.40	3299	0.7
0.50	3292	0.9
0.60	3284	1.1
0.70	3277	1.3
0.80	3270	1.5
0.90	3263	1.7
1.00	3256	1.9
1.10	3248	2.1
1.12	3247	2.1
1.20	3241	2.3
1.30	3234	2.5
1.37	3229	2.6
1.50	3220	2.9

**Table 3:** Calculated Raman bands of ice VI after Abebe & Walrafen (1979) as a function of pressure (P) at ambient temperature (294 K).

 $3324 \text{ cm}^{-1}$  at a pressure of 0.05 GPa and ambient temperature as initial position (Table 3). The comparison of the calculated with the measured bands from the experiment shows a deviation of the values from each other. In the Raman measurements carried out, the ice VI band has an average position of 3229  $\text{cm}^{-1}$  after deconvolution with the Fityk program. According to the calculations, this would correspond to a pressure of about 1.37 GPa at ambient temperature, which is in the field of crystallization of ice VI. The Raman double band at about 3400 cm<sup>-1</sup> represents the stretching vibration of the hydrogen bond, which affects the interatomic distance along the bond axis of the OH group (Walrafen et al. (1986)). Accordingly, the stretching vibration is assumed not to have changed its nature (mode) during the phase transition from water to ice. Only the energy required to excite the vibration of the OH pairs changes, i.e. the parameters represented by the Raman spectrometer. If one assumes that the data from Abebe & Walrafen (1979) for ice VI also apply to water (Tab. 3), then the shift of about 77  $\text{cm}^{-1}$  would correspond to a difference of 1.12 GPa (corresponding to 187 bar). This pressure would be equivalent to the generated pressure, displayed by the hydraulic pump (180 bar). The determined shift to higher wavenumbers is therefore interpreted only as an effect on the pressure drop. According to these Raman measurements, a calibration based solely on the band position of ice at a set pressure is not feasible. In the future, Raman spectra should be recorded already at the beginning of the experiment with successive increase of the pressure. These measurements would represent how the band positions shift as a function of pressure, first of water and later of ice. The measured values

could then be compared with the reported band shifts from ice VI to Abebe & Walrafen (1979). In addition, a pressure determination with a ruby fluorescence gauge is essential to obtain unbiased values.

#### IV.2.4.2. Calibration of the D-PEC

I provided the first in-situ spectroscopic experiments to investigate the pressure performance of the newly designed Diamond-windows Paris-Edinburgh Cell. The D-PEC operates as a uniaxial press, compressing the sample volume to generate high pressures, similar to the DAC. The lower piston moves upward to minimize the space between the pistons, thereby reducing the sample volume. Therefore, we chose a calibration that was already established for the DAC system. In general, there was a linear correlation between the pressure exerted by the oil pump and the calculated pressure of the samples, which was derived from the peak shifts in the fluorescence and Raman measurements. This calibration series demonstrated a successful agreement between the calculated sample chamber pressure of quartz and ruby, with almost a 1:1 ratio. However, there were several outliers that require further discussion. Before going into detail about the obtained data, it is crucial to discuss the general experimental setup and procedures. The spectroscopic observations were obtained by making measurements through the diamonds. The design of these one-sided spherical diamonds was quite challenging as the rounded surfaces can slip during their insertion in the tungsten carbide anvils. Aligning the spherical diamonds with a table face parallel to the anvil proved to be time-consuming, requiring numerous attempts at gluing the diamonds. Additionally, the diamonds can slip during the pressure increase, resulting in damage to the anvils. After the experiment there was an imprint of the edge of the lower diamond in the concave seat of the tungsten carbide seat visible. The slipping and the imprint favors that the diamond or the anvil break and shortens their lifetime. In this calibration series, the lower tungsten carbide anvil experienced a central crack, whereas the upper anvil showed signs of several scratches.

In general, there are significant differences between the DAC and the D-PEC in terms of sample chamber volume and gasket deformation. During the initial pressure increase in the D-PEC, a greater quantity of gasket material (4.6 g) was compressed (in comparison to the DAC, with less than 0.5 g) and the force exerted by the oil pressure is primarily transferred to the deformation of the gasket material. Furthermore, the gasket is composed of two distinct materials, namely silver and steel, and exhibits a more intricate shape, comprising a double cone and toroid configuration (in comparison to the DAC, with a cylindrical gasket shape). While the DAC uses the diamonds as pressure intensifiers, here they act as windows. In the D-PEC, the tungsten carbide anvils reduce the sample chamber ( $\emptyset$ : 2.5 to 1 mm) (Figure 26). The piston movement reduces the thickness of the outer part of the steel gasket from 3.3 mm to approximately 1.5 mm. The diameter of the steel-silver gasket increases up to 25 mm (+65%). The sample chamber decreased from 2.5 mm to 1.0 mm in diameter, and in

length from 6 mm to 5 mm. As the data show, the closing pressure is not trivial. Up to about 100 bar, both gauges show lower calculated pressure values than expected from their trend lines.



Figure 26: Steel-Silver gasket assembly after the experiment with zoom into the sample chamber. (1) ruby and (2) quartz.

The good agreement between the ruby and the quartz data indicates that ruby heating was minimal. The fluorescence signal of the ruby showed high intensities and could be measured at almost any depth along the 2-3 mm length of the sample volume. Both signals, fluorescence and Raman, become more distinct at higher pressures. For ruby at 694 nm, the fluorescence signal intensity reached approximately 3500 a.u. at 20 bar, and it increased to 4300 a.u. at 700 bar (+20%). In contrast, the quartz Raman signal at 464 cm<sup>-1</sup> showed an intensity of 1900 a.u. at 20 bar, which increased to 4100 a.u. at 700 bar (+46%). The higher intensities may be due to the sample chamber becoming narrower and more compact. The silver chamber surface may reflect the laser signal more strongly. Due to the setup design, spectroscopic measurements at 0 bar are not available for the pressure-increasing path. The quartz, ruby, and methanol and ethanol mixture must be loaded into the steel-silver gasket while the D-PEC is in a vertical position. The sample chamber was sealed at 20 bar before the D-PEC was positioned horizontally to align it with the spectroscopic setup (LDM and SuperHead). The final measurement taken at 0 bar on the descent path was chosen as the ambient pressure reference. For ruby the peak position at 0 bar and at 20 bar oil pressure is the same. However, for quartz the the 464  $cm^{-1}$  band shifts 0.08  $cm^{-1}$ , representing a sample pressure of 0.01 GPa at 20 bar. Schmidt & Ziemann (2000) calculated pressure using quartz Raman lines as shifts relative to the reference frequency at 300 K and 1 bar. With the exception of the first 50 bars and the last 200 bars, the oil pressure increased

systematically in 15-bar intervals. with subsequent breaks of 12-26 minutes between each pressure increase and fluorescence and Raman measurements. During the two-day test series, the lead scientists took several breaks that interrupted the progression of the pressure increase. During these pauses, a decrease in the calculated sample pressure was observed at oil pressures of approximately 180 bar and 280 bar (as indicated by the grey bands in

Figures 20-22). Measurements were taken at 35-minute intervals between 160 bar, 175 bar and 190 bar. Additionally, a cracking sound was heard when the pressure reached 160 bar. The cracking sound may have been caused by the brittle expansion of the steel gasket (Figure 26). Multiple alignment of the focal plane with the spectroscopic setup was required for the conducting the Raman measurement of quartz. At an oil pressure of 190 bar, the working distance of the LDM and SuperHead had to be extended by 540  $\mu$ m. This refocused the focal plane of the laser signal onto the first diamond that the signal enters, reducing the length of the sample chamber. The lowest pressure drop was observed at 280 bar during the night break. A second measurement was taken after 16 hours 27 minutes, when the oil pressure dropped to 272 bar (-3%). Again, a refocusing of 72  $\mu$ m to the center of the sample chamber was necessary.

In particular, the results for quartz below 2.1 GPa are in good agreement with data available in the literature (Schmidt & Ziemann (2000)). Further experimental data are required to provide a valid interpretation of the higher-pressure measurements, which extend beyond the currently available literature. However, the calculated pressure for quartz and ruby is consistent (see Figure 22) and suggests an application of the quartz pressure calculation above 2.1 GPa.

The data obtained in this study with the frequency shift against the calculated pressure are an excellent continuation of the data of Schmidt & Ziemann (2000) at 296 K (Figure 27).



**Figure 27:** Frequency shift of the 464 cm<sup>-1</sup> Raman line of  $\alpha$ -quartz as a function of pressure. Red dots show data of Schmidt & Ziemann (2000) at 296 K.

The highest measured peak shifts for ruby and quartz were at the oil pressure of 700 bar. The highest recorded oil pressure corresponds to the calculated pressure of 5.1 GPa for ruby and 4.4 GPa for quartz. The pressure was increased to 700 bar in just 14 minutes after reaching 620 bar. This corresponds to a fivefold increase in half the time of the previous pressure increase steps. The gasket assembly deformed rapidly, which may have prevented the pressure gauge from relaxing adequately. The measurements suggest that the quartz took longer to equilibrate than the ruby, resulting in a slightly lower calculated pressure for the quartz. This effect is particularly noticeable at the highest-pressure data points. The larger dimensions of the quartz may also affect its peak shift behavior. Internal stress/strain may have caused different zones within the quartz as a result of the compression of the sample chamber walls. In fact, the quartz sample in the D-PEC is at least twice the diameter and 50 times the length of a sample in the DAC.

Another potential explanation for the observed inconsistency in the assumed pressure at 5 GPa in the sample chamber is the press frame of the D-PEC. The Paris-Edinburgh press frame made of steel (35NiCrMo16) could soften under pressure and deform under strain. The design of the D-PEC may also have an effect on the sample pressure. The sudden drop in pressure observed in both ruby and quartz at 590 and 570 bar may be due to the viscoelastic behavior of the D-PEC frame. The press frame, is expected to exhibit viscoelastic behavior.

Under increasing pressure, the frame is expected to stretch before stiffening over time (if no further pressure increase occurs). The viscoelastic effect would be more pronounced at high pressures. When measurements are taken more frequently, the frame is expected to have greater stiffness than when it exhibits more viscoelastic behavior.

Once the pressure reached approximately 5 GPa in the sample chamber, the oil pressure was released as slowly as possible. It was not possible to select exact oil pressure values, as the oil was drained manually via a two-stage valve system, with the oil in the hose in between acting as a buffer. The pressure release path also shows an effect of the deformation of the sample chamber. During the 100 bar/step pressure drop, pressure measurements were taken every 30 minutes. The data indicate a hysteresis in the sample chamber during the pressure decay path, with the calculated pressure following a curved shape. The parabolic trend shows approximately 1.0-1.5 GPa higher calculated pressures, as do the corresponding values for the increasing pressure path. This may indicate residual pressure in the minerals. The gasket assembly is less pressure transmissive than in the ascending pressure path and retains residual pressure within the chamber. This is due to the geometry of the gasket. As the steel becomes more brittle, it confines the silver and prevents it from spreading further.

#### IV.2.5. Conclusions

This was the first successful attempt to determine the sample pressure of a D-PEC, given the successful cross-calibration with spectroscopic measurement of ruby and quartz. For future in-situ experiments, ruby can be used as a standard pressure gauge. The main suggestions to improve the future application of the D-PEC are:

- The insertion of one-sided spherical diamonds is a challenge, with the additional risk of the rounded surfaces to slip out of the anvil. Therefore, conical diamonds, similar to those used in a DAC, such as the Böhler-Almax design were suggested for future experiments.
- The increments of 15-bar oil pressure steps are considered to be too narrow. Subsequent experiments could explore wider steps in pressure increase for a more comprehensive investigation.

# V. Development of a high temperature gasket for the D-PEC

The spectroscopic and optically open sample chamber with diamond windows requires several adaptations for high temperature applications. The failed designs of a HT gasket for the D-PEC are presented below. After that, the final design and its manufacturing process is documented in section VI.3.4.

## V.1. First designs for a high temperature gasket

Various coatings were applied to the steel gasket used at ambient temperatures (see Figure 28a). For the electrical insulation of the gasket against the anvils, different coatings were tested, e.g. citrate, iron oxide, talc, thermal varnish (Supertherm 800°C, Dupli-Color, Haßmersheim) and a MgO adhesive (Resbond 919 Powder, Polytec PT, Karlsbad). Figure 28a shows the cracks in the thermal lacquer caused by piercing the steel. Despite repeated rounding of the edges of the gasket (Figure 28b), the steel always cracked the coatings. For the Teflon-steel-polypropylene assembly, also a Teflon tape was glued over the rounded steel gasket. The Teflon ring flowed all over the entire gasket, surrounding it until the steel pierced through with increasing pressure. The Teflon gasket appeared extremely labile because it got deformed easily (Figure 28c). For the polycarbonate-resin-salt assembly, the confining polycarbonate ring deformed irregularly (Figure 28d). The CaldoFix2 (Struers ApS, Ballerup, DK) resin was too brittle and got overflown by the salt. A loose salt core was put in the center of the gasket and a polycarbonate ring around another resin (Epo-Tek®353ND, Epoxy Technology, Billerica, US) ring (Figure 28e). With increasing pressure, the resistance increased too until "overflow" at around 4.7 kbar. The experiment was canceled at around 8 kbar, because it was possible that not enough salt was used making the salt core, so that the anvils could touch and burst again. A ratio of 5 parts resin and 1 part boron by weight hardened for 1 hour at 353 K and was processed as ring (Figure 28f). The PC ring had dimensions of 20.0 x 1.5 mm. The gasket deformed completely ductile. Salt was pressed into small cracks of the resin and overflowed the resin ring. The resin pushed against the polycarbonate ring and stretched it radially. The gasket pressure was reached 20 kbar.

The materials commonly used for HT gaskets, such as Teflon and epoxy resin, proved to be either too ductile or brittle to withstand the pressure. For the gasket in the D-PEC, all of these materials have failed as gasket before reaching 5 GPa. Further descriptions of the experimental setup and details about the tested materials are documented in the master's thesis by Friedrich (2019).



**Figure 28:** Photos of a) polypropylene-coated steel gasket, b) Teflon-Teflon tape on rounded steel gasket-polypropylene gasket, c) Teflon-salt gasket, d)-f) polycarbonate-resin-salt gaskets. (1) Steel, (2) thermal varnish coat, (3) polypropylene, (4) Teflon ring, (5) Teflon tape, (6) salt, (7) resin (CaldoFix2), (8) polycarbonate ring, (9) resin (Epo-Tek®353ND) and (10) resin (Epo-Tek®353ND) with boron powder. Black bar indicates 1 mm.

# V.2. CuBe-NaCl gasket

The first design used for in-situ experiments at HT with the D-PEC was the CuBe-NaCl gasket assembly. The HT gasket assembly has an onion-like structure. All components of the HT gasket must be prefabricated, as it is assembled from the outside in. The manufacturing process is documented in chronological order: First the CuBe gasket is prepared, then the NaCl gasket and finally the internal heating components.

#### V.2.1. CuBe gasket

During my research stay, I learned fabrication techniques from the co-developer of the Paris-Edinburgh press, Dr. S. Klotz. He developed the sandwich gasket (Klotz et al. (2008)). I adjusted the design of the sandwich gasket to the curves of the open single-toroidal anvil with diamond window (Figure 29).



Figure 29: Drawing a) and half section b) of the rounded CuBe gasket with MgO adhesive. Black bar indicates 1 mm.

A copper beryllium rod (C17200, Ø: 15 mm, Metallbearbeitung Maier, Pfaffenhofen) was turned into two half-round rings, on a metal lathe under cooling with a lubricant. Then the CuBe rings were hardened in an oven at 561 K (288 °C) for 30 minutes (Klotz (2012)). To prevent a short circuit during internal heating, this single-toroidal gasket consists of two half rings with a layer of ceramic adhesive (Resbond 919, Final Advanced Materials GmbH, Freiburg) between them (Klotz et al. (2008)). The MgO powder (temp. range <1800 K) was liquefied with distilled water (<5%), in order to achieve a honey-like viscosity. The ceramic glue was applied to the flat side of one CuBe half ring, assembled with the second, and then dried for 24 hours at ambient temperature. Excess ceramic adhesive was ground off with a rotary tool.

#### V.2.2. NaCl gasket

The curved shape of the single-toroidal anvils and the desire to insert a liquid first pressure transmitting medium (for hydrostatic conditions) require a preformed gasket to seal the connection to the diamond window. Since halite cannot be lathed, two press die sets were developed to pre-form the HT inner gasket and assemble it with the confining gasket. I designed the two press tools and had them manufactured by Hawedia from tungsten carbide. Both tools are used with an ordinary workshop press, one for shaping the inner gasket and another for assembling the inner gasket and confining gasket. The workshop press consists of a H-frame (XLP256P392U, 25 Ton, Enerpac) with a single-acting cylinder (RC256, Enerpac) and hydraulic hand pump (P392, Enerpac, Menomonee Falls, US). For the use of the press die sets with the workshop press, the in-house precision workshop manufactured accessories that I designed. Special aluminum attachments have been developed to taper the pressure surface of the hydraulic piston of the workshop press so that it can exert pressure to the plunger of the prepressing tools. To drill and lathe the HT components with millimeter precision, drilling and grinding jigs were manufactured. I milled (micro miller MF 70, Proxxon, Föhren) and turned the parts on a precision lathe (SD 300, Proxxon, Föhren). A standard rotary tool (4000, Dremel, Racine, USA) with suitable attachments was used for grinding, polishing and parting the lathed components. To shape the inner gasket, I developed a press die set that compresses the salt powder. The carbide tool consists of a cylindrical die (OD25xID9.8x60 mm, ha20180703) (1) to hold the pressure and two plungers (Ø9.8x16 mm, ha20180704) (2, 3) that apply the pressure (Figure 30). The die has an inner diameter of 9.8 mm, corresponding to the inside diameter of the CuBe gasket, i.e. the space for the inner gasket. The plungers reproduce the exact negative shape of the open single-toroidal anvils with diamond windows.



**Figure 30:** Photo of prepressing tool with die in a) side and b) top view. c) Internal heating components. (1) Die, (2,3) plunger, (3,4) pre-compressed salt gasket, (4) drilled salt gasket, (5) CuBe gasket, (6) graphite, (7) ceramic and (8) silver. Black bar indicates 1 cm.

The salt powder (99.5% sodium chloride, CAS 1064045000, Merck, Darmstadt) is mixed 5% distilled water and then ground in an agate mortar to homogenize the mixture. The additional water ensures uniform plastic deformation and homogeneous recrystallization into the desired shape of the inner gasket, a salt double cone. After one plunger is inserted into the die sleeve, about 0.6 g NaCl powder is filled and sealed with the second plunger on top (NaCl: OD: 9.0 mm, ID: 3.7 mm, height: 6.6 mm in the center, height: 3.0 mm at the edge). For an application with a thermocouple ( $\emptyset$ : 0.05 mm; CHAL-002, Omega Engineering, Deckenpfronn) inside the inner gasket, the amount of salt powder must be divided into two equal parts. After filling the first 0.3 g NaCl, a thin mica disc ( $\emptyset$ : 9.5 mm) is inserted in the die to divide the salt cell so that the thermocouple can later be inserted between the two halves. Then the second half of the salt powder is poured in and sealed with the second plunger. The preformed split salt gaskets are shown in figure 31.



**Figure 31:** Photo of a) side and b) top view of prepressing tool with split NaCl gasket. (1) Die, (2) plunger and (3) pre-compressed split salt gasket. Black bar indicates 5 mm.

The die and plunger enclosing the salt powder were positioned centrally on the hydraulic press. The piston exerts uniaxial pressure via the plunger, causing the salt grains to deform and recrystallize as inner gasket. The pressure is slowly increased to 100 bar and maintained for 2 minutes, corresponding to a pressure of 6.5 tn. The pre-compressed salt gasket is placed in a drilling jig and drilled with a carbide drill bit ( $\emptyset$ : 3.5 mm), so that space is created for the sample and heating components (Figure 31, 3). For the best results, the cylinder bore in the inner gasket should be ground and polished. In this process, a rotary tool with attached aluminium oxide grinding stone and later a polishing wheel were used to smooth the bore.

This results in a very smooth and accurate symmetrical bore with a significantly hardened surface that improves performance and sealing under pressure.

#### V.2.3. Internal heating components

The internal heating system consists of a stack of three thin tubes machined to fit into the polished hole in the pre-compressed NaCl gasket. One cylinder was made of graphite and two other smaller ones of ceramic and metal to protect the sample. The heating process was controlled by the graphite tube, the outermost cylinder. A small tube (OD: 3.6 mm, ID: 2.8 mm, height: 5.0 mm), the actual oven, and rings (OD: 4.0 mm, ID: 2.8 mm, height: 1.0 mm) were turned from a graphite rod (Müller & Rössner GmbH, Niederkassel) on a lathe. The graphite rings were the electrical contacts between the heating tube and the metal anvils. An insulating ceramic tube stored the heat and protects the sample from the brittle detachment of the graphite during pressure generation. The Degussit AL23 ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) (OD: 2.8 mm, ID: 2.2 mm; Friatec-Keramik, Mannheim) was cut to a length of 4.5 mm and the edges are ground manually. A noble metal tube, the innermost cylinder, reduced chemical contamination of the sample (as it is chemically inert) and stabilized the sample chamber against the more brittle ceramic and graphite. The temperature distribution in a gold capsule is much more homogeneous than in a sample chamber without one (Schilling & Wunder (2004)). Since the thermal conductivity of graphite lies between the values of gold and NaCl (or the ceramics used), the temperature gradient in a graphite capsule is higher than in a noble metal capsule (Schilling & Wunder (2004)). (The same should be true for silver, as it has an even higher thermal conductivity than gold.) In the following feasibility tests and initial test experiments, gold is replaced by silver, because it has similar electrical and thermal properties but is significantly cheaper. The silver tube was cut to the appropriate length (OD: 2.0 mm, ID: 1.8 mm, height: 4.0 mm; Heraeus, Hanau). The stack of tubes was assembled from the inside out. To bring the tubes to the exact diameter and height, the outer surfaces and edges must be ground and smoothed by hand after precision turning. First, misalignments and rough remnants were cut off with a rotary tool and attached carving bit. Pointed edges and chips were removed manually with fine sandpaper (<18  $\mu$ m). Before further assembly, the ceramic and metal tube were cleaned in an ultrasonic bath for 15 minutes. First, the silver tube was inserted into the ceramic tube and pressed against the ceramic. The edges of the silver tube were placed over the ceramic using a needle. Then both tubes were slid into the graphite tube. Finally, the entire stack of tubes was clamped into the NaCl gasket. All manufacturing was performed at ambient temperature.

#### V.2.4. Gasket assembly tool

The assembly tool is also a press die set. In conjunction with the hydraulic workshop press, it puts the pre-compressed inner gasket together with the confining gasket, ready for inserting the sample. This press tool is required to fill the sample chamber with a liquid first pressure transmitting medium. The cylindrical die (OD: 80 mm, ID: 16 mm, height: 60 mm; ha20200200, Hawedia) is a protective feature that holds the inner gasket and gasket together during pressure build-up. The die encloses a lower plunger (OD: 16 mm, height: 16 mm; ha20200202, Hawedia), which has a hemispherical indentation for the diamond (like the open single-toroidal anvil), and a two-part upper plunger (Figure 32 and Appendix Fig. 76. The upper plunger is divided in an outer cylinder, a guide sleeve (OD: 16 mm, ID: 9.8 mm, height: 16 mm; ha20200201, Hawedia), and an inner part, the actual plunger, which is the same (ha20180704, Hawedia) as for the prepressing tool.



**Figure 32:** Photo of gasket assembly tool with CuBe-NaCl gasket. (1) Die, (2) lower plunger, (3) guide sleeve, (4) upper plunger and (5) CuBe-NaCl gasket. Black bar indicates 5 mm.

Before assembling the HT gasket, a ceramic glue (MgO adhesive, which was also used for the CuBe gasket) was applied with a needle to the interface between the silver and the ceramic tube. Without ceramic glue, the silver can act as a conductor and heater for the applied current by coming in contact with the anvil. The inner gasket was moistened with water, as a slight dissolution of the salt facilitates merging. The gasket assembly tool merged the confining gasket with the salt gasket and the lower diamond to seal the chamber downward. For this purpose, the pre-compressed salt cell with HT inserts, the prepared sandwich gasket and a diamond were placed on the lower plunger. Then everything was inserted into the die. The guide sleeve, which holds the gasket in position and prevents its deformation, was

placed on the HT gasket assembly. The second plunger was inserted and a pressure of 50 bar was applied, which slightly compresses the salt cell and the inserted HT components with the diamond. It is important to build up the pressure slowly (2 minutes), hold it for at least 1 minute and then release it slowly (30 seconds) to avoid cracks in the salt gasket or especially in the HT assembly as graphite and ceramic are brittle. The pre-compressed salt gasket was pressed firmly into the CuBe gasket and the diamond adheres to it. At this point, the HT gasket assembly with the lower diamond windows can be filled with a liquid pressure transmitting medium and a sample and is ready for heating (Figure 33).



**Figure 33:** a) Exploded view and b) photo of open single-toroidal anvils and CuBe-NaCl gasket with diamond windows under pressure. (1) Open tungsten carbide anvil, (2) one-sided spherical diamond, (3) CuBe gasket, (4) NaCl gasket, (5) graphite heater, (6) ceramic, (7) silver, (8) PTM (water) and sample. The black bar indicates 1 mm.

#### V.2.5. External temperatures of HT-D-PEC without cooling system

First feasibility tests with the HT setup were conducted with the HT-D-PEC. For the following experiments the new HT gasket was tested with its heating set up (copper ring clamp connected to the power supply SM 15-400). Heating was performed with an SM 15-400 power supply (Delta Elektronika, Zierikzee, NL), which provides current with an output of up to 15 V and 400 A (equivalent to 6 kW). The DC laboratory power supply is highly sensitive for precise and stable voltage and current regulation (with 10-turn potentiometers), thus enabling controlled and consistent heating. The generator used was mounted in a 19-inch rack, together with a power controller (SE0040 M0306, Schulz Electronics), a temperature control unit (3204 and 3208, Eurotherm, Worthing, UK) and two other power supplies (SM 70-90 and SM 18-50, Delta Elektronika) connected for illumination of the sample chamber. A low supply line resistance ensures an exclusive heat dissipation inside the sample chamber. Therefore, the designed connecting elements, the ring clamp and screws, consist of materials with low electrical resistivity, like copper and brass ( $1.68*10^{-8} \Omega m$  and  $0.6-0.9*10^{-7} \Omega m$  at

293 K). A setscrew and two hex nuts (M12) made of brass secure each cable lug to a ring clamp (Figure 34, 3).



**Figure 34:** a) Photo and b) half section of the modified HT-D-PEC. (1) Transport frame, (2) brass cooling sleeve, (3) copper ring clamp, (4) pump valve, (5) axial channel, (6) PVC-Ring, and (7) hydraulic ram. The red frame highlights the gasket-anvil assembly.

To maintain the compactness of the D-PEC, a combination of a power supply connector and an external sleeve for a heat transfer fluid was designed. The newly developed copper ring clamp is attached to the cooling sleeve with a locking screw and encloses the anvils of the D-PEC. The copper clamp resembles a large eye bolt and functions as a retaining ring for the massive cables. Two massive copper cables connect the cable lug of the SM 15-400 power supply to the D-PEC. The power supply generates the electric current that flows to one cable and passes through the copper clamp, anvils and to the sample chamber. At that point, the graphite tube inside resists the current flow, resulting in internal resistance heating. Then the current continues to flow through the second anvil and second copper ring (and cable) and back to the power source to complete the circuit. The rest of the press body, which is not heated and is not part of the electrical circuit, must be insulated against the resistance heating. In addition, the hydraulic oil in the cylinder of the D-PEC should be protected against all electrical overloads and short circuits. An insulating ring made of PVC (plastic insulator) surrounding the lower piston prevents the current flow towards the cylinder (Figure 35, 4). Also, a plastic disk (polypropylene) with a hole for the rear channel is inserted under the lower piston. Before each HT experiment, lubricant grease should be applied between the anvils and backing plates of the pistons to prevent them from sticking together due to the expansion of the materials during heating.



**Figure 35:** Photos of the newly constructed add-ons for the HT-D-PEC in a) top and b) side view. (1) Brass cooling sleeve, (2) copper clamp, (3) brass hex nut, and (4) insulating ring. The black bar indicates 3 cm.

The HT gasket was manufactured and prepared as in section V.2 described. The temperature was measured using thermocouples and an infrared thermometer. First the general heating process of the press was recorded to specify the heat transfer without cooling of the D-PEC body. The brass sleeve was unfilled to define the general homogeneity of the heat distribution of the HT-D-PEC and to determine at what temperature the press body needed to be cooled. The copper ring clamp was attached to the lower anvil (cylinder side) on the empty brass sleeve. Due to design and manufacturing defects, the upper brass cooling sleeve (upper sleeve 22 ml; lower sleeve 28 ml) and upper copper ring clamp could not be connected. Therefore, the second power cable was bolted into the M6 screw hole on the top of the press body. This connection on the top provided more space for loading the gasket than with both copper clamps and brass sleeves around the pistons. Measurement points for an infrared thermometer (IR-750-EUR, Beha-Amprobe, Glottertal) were drawn on the D-PEC (approx. 50 measurement points in total). The deviation for the IR thermometer is 1.8 K or 1.8% of the measured value (whichever is greater). Furthermore, a K-type thermocouple was used, which was attached to the thermometer. Around 30 K-Type thermocouples (0.3 mm diameter; Heraeus, Hanau) were glued to the entire press body (Figure 36b). The thermocouples made of NiCr-Ni were insulated with a ceramic (Degussit23) near the hot junction and with plastic sleeves behind it. Boiling water (373 K) and a water-ice mixture (273 K) were used for the temperature calibration of the thermocouples. The maximum temperature deviation of the thermocouples is the greater value of 2.2 K or 0.75% (after DIN EN 60584-1:2014-07; IEC 60584-1:2013). The temperature was measured with thermocouples and an IR thermometer. Further experimental description is documented in the Bachelor thesis by Reuther (2019).



**Figure 36:** a) Drawing and b) photo of HT-D-PEC with thermocouples and measurement points for IR thermometer. (1) Brass screw, (2) copper clamp, (3) brass sleeve, (4) plastic insulator, (5) thermocouple, and (6) DC power supply. The black bar indicates 5 cm.

The HT sample chamber was filled with water as pressure transmitting medium and pressurized to 1 GPa. After pressurization, the HT-D-PEC was heated with 10 W per step within a 20-minute interval. The high temperatures were generated by resistance heating, with an electric current of typically 150 A passing through the graphite furnace. The typical time required to increase and decrease the temperature in the HT-D-PEC was 20 and 60 min, respectively. One HT gasket assembly lasted more than 40 hours with repeated overnight heating. The temperature was documented at the anvils, axial channel and outer press body. The temperature closest to that of the gasket was documented by the thermocouple (of the IR thermometer) near the diamond, which was inserted from both sides through the D-PEC channel (Figure 37; aperture front and back).



**Figure 37:** Comparison of different temperature measurement points of the HT-D-PEC with supplied electrical energy during the heating process.

Voltage and current of the thermocouple were measured after 10 s of the HT-D-PEC operation and every 30 s thereafter at constant heating power. In general, the heating process and heat transfer was evenly and homogeneously distributed in the press body. The components near the graphite heater, such as the diamond, channel and anvil, were (inevitably) hotter than other parts. Therefore, it can be assumed that the highest temperature was generated inside the sample chamber and no further (or higher) resistance was generated. After about 30 hours of operation, the resistance dropped from 0.03  $\Omega$  (graphite) to 0.004-0.006  $\Omega$ , indicating a change in the current flow within the heater (Figure 37). The drop in temperature (about 25-30%) happened due to a change in the arrangement of the sample chamber and graphite heater. The silver probably bonded with the anvils and acted like a heater, which could result in lower heating performance. Controlled heating cannot be guaranteed with resistance heating by the silver. The diamond could be exposed to excessive heat, shortening its lifespan. Nevertheless, the HT gasket assembly was stable enough to continue the heating process even 10 hours after the structural failure of the heater. In the subsequent heating processes, the temperature inside the sample chamber should also be monitored. In order to determine the temperature of the sample more accurately, the inner gasket should be divided and a thermocouple inserted near the graphite heater in the subsequent HT experiments.

# VI. Development and calibration of the High Temperature-diamond windows-Paris-Edinburgh cell with a NaCI-CuBe gasket assembly

# VI.1. Introduction

In Earth and materials science, it is desirable to cover a wide temperature range with a high-pressure instrument, including all representative P-T conditions in the interior of Earth. Until now, no high-pressure device for macroscopic sample volume exists for in-situ measurements under high temperatures. There are only non-transparent large-volume presses, such as the piston cylinder press (with maximal P < 6 GPa, T < 2000 K, sample sizes < 200mm<sup>3</sup>) or multi-anvil press (with maximal P < 90 GPa, T < 2500 K, sample sizes < 100 mm<sup>3</sup>) (Müller et al. (2006) and reference therein; Klotz (2012)). For in-situ measurements under high pressure and high temperature, the diamond anvil cell is the most commonly used instrument. However, the DAC is limited to its microscopic sample volume (with maximal P < 460 GPa, T < 7000 K, sample sizes  $< 300 \mu$ m) (Dubrovinskaia et al. (2016); Alabdulkarim et al. (2022)). Some modified large volume presses with one diamond windows exist, but these are not heated and limited to 1 mm<sup>3</sup> (Lipp et al. (2005)). The newly designed high temperature-diamond windows-Paris-Edinburgh Cell (HT-D-PEC) provides in-situ conditions with pressures up to 6 GPa at temperatures up to 1000 K for sample volumes up to 10-30 mm<sup>3</sup>. Such P-T conditions correspond to the geothermal gradient in the upper lithosphere. Therefore, this HT-D-PEC combines the in-situ possibilities of a diamond anvil cell with the sample volume and P-T condition of a large volume press.

The following section provides an overview of the development and improvement of the high temperature gasket and sample chamber assemblies of the HT-D-PEC. A pure metallic gasket, used for ambient temperature setups, was not suitable for high-temperature experiments because heating was achieved through resistive methods. Therefore, an insulating and temperature resistant gasket assembly with two diamond windows had to be developed. Various materials such as salt, plastic and pyrophyllite and their different dimensions have been tested. A number of high-temperature gaskets have been evaluated with a particular focus on their temperature and pressure resistance. The applied voltage and the corresponding power output were correlated. The primary objective was to establish a correlation between the heating power supplied by a high-voltage source and the resistance heating of the furnace, which affects the sample volume. Additionally, thermocouples were employed to monitor the internal temperature within the sample chamber.

Engineered for in-situ HP and HT experiments, the two final gasket-sample chamber assemblies performed pressures up to 6 GPa and temperatures up to 1000 K. There is a gasket assembly with and without an inserted glass window. Using in-situ fluorescence and Raman

measurements, the sample chamber pressure was calibrated against the oil pressure exerted on the piston. This rough calibration was juxtaposed with the pressure calibration at ambient temperature to identify any discrepancies in the pressure behaviour of the different gasket assemblies of the D-PEC (refer to section IV.2.3.2.).

# VI.2. Methods

### VI.2.1. Experimental setup

Pressure was applied using a hydraulic oil pump (P2232, Enerpac) with a digital pressure sensor (P105 and alpha-c, FGP Instruments). The Paris-Edinburgh press with diamond windows was combined with a heating setup for the sample chamber and a thermostat to cool the press body.

#### VI.2.1.1. Heating setup

The heating setup consists of a power supply (SM40-500, Delta Elektronika, NL). The power supply had cables, 3 m long and 12 mm in diameter. The copper cables were connected with customized copper spoons (12 mm thick; in-house precision mechanics workshop) to the new cooling anvils (Figure 38, 2 and Appendix Fig. 77 and 78). The power supply was set to specific voltage values, typically in 0.25 V increments and 0.10 V increments. The cooling anvil, filled with approximately 7 ml of cooling water, was tested using 8 bar, although 4 bar is typically applied as standard. The refrigerated circulating thermostat bath (Proline RP 845, Lauda, Lauda-Königshofen) cooled the water down to 288 K. Cool-down times were not necessary, as the entire press body (except the anvils and gasket assembly) remained at ambient temperature during heating.

To insulate the HT gasket assembly from the press body, plastic sleeves were mounted around the anvils (see Appendix Fig. 79 and 80).

The thermocouples made of NiCr-Ni (0.3 mm diameter; Heraeus, Hanau) were insulated with pyrophyllite and a ceramic near the hot junction. Boiling water (373 K) and a water-ice mixture (273 K) were used for the temperature calibration of the K-type thermocouples. The maximum temperature deviation of the thermocouples is the greater value of 2.2 K or 0.75% (after DIN EN 60584-1:2014-07; IEC 60584-1:2013).

Development and calibration of the High Temperature-diamond windows-Paris-Edinburgh cell with a NaCl-CuBe gasket assembly



**Figure 38:** a) Photo of the HT-D-PEC. b) Half section of the HT-D-PEC. (1) Alumina sheathed thermocouple, (2) cooling anvils with connection, (3) Cu-spoon and (4) plastic sleeve. Black bar indicates 50 cm.

#### VI.2.1.2. Spectroscopic setup

The setup consists of the spectroscopic components mounted behind the channel of the HT-D-PEC and its gasket assembly. Attempts were made to take the spectra of the samarium-doped strontium borate, ruby and quartz at the same spot in the sample chamber in order to obtain a reliable comparison between the pressure shifts.

#### VI.2.1.2.1. Fluorescence setup in Heidelberg

A portable spectrometer (HR-4VIS500-10, Ocean Insight;1200 g/mm, slit= 10  $\mu$ m, 0.48 nm resolution) was inserted with a glass fiber (Ocean Insight;  $\emptyset = 100 \ \mu$ m) in the axial channel of the HT-D-PEC. The 523 nm line of a common laser diode (LM05GND Tru components; Conrad Electronic SE, Hirschau) with maximum power of 5 mW excited fluorescence signals from the samples.

#### VI.2.1.2.2. Raman setup at GSI

The spectroscopic setup consisted of the long-distance microscope (LDM) screwed to the Raman probe (Vishead, Horiba; f = 40 mm) with a customized adapter. The Raman probe was connected to the spectrometer (iHR 320, Horiba; f/4.1, 1800 g/mm, CCD camera 1024x256 pixel) via a glass fiber (Ocean Optics;  $\emptyset = 100 \mu \text{m}$ , L = 10 m). A green laser (Sapphire, Coherent; 532 nm, used 20-30% of 100 mW, Noise/Power Stability: <0.8% RMS) excited the fluorescence and Raman signals. The spectrometer, the Raman probe and the laser were used in the Raman laboratory at GSI in Darmstadt.

#### VI.2.1.3. Data processing

All fluorescence and Raman peak bands were fitted with the pseudovoigt function (Syassen (2008)). The symmetric Raman bands of mineral crystals and non-aqueous fluids are best fit using Gaussian–Lorentzian profile (X. Yuan & Mayanovic (2017)).

#### VI.2.1.3.1. Fluorescence measurements obtained at Heidelberg

For the data processing of the data obtained by the HR-4VIS500-10 spectrometer, the program Fityk was used (Wojdyr (2010)). The linear background was set at 680 nm and 720 nm. The fitted area was 683-710 nm. In the measured spectra, the strontium borate  ${}^{5}D_{0}{}^{-7}F_{0}$  band exhibited an asymmetric peak shape, caused by the spectrometer. Therefore, the peak maximum was set in accordance with the FWHM, as assumed with a symmetrical peak shape. For the sample pressure calculation from the peak shift of strontium borate and ruby, the formulas in section VI.2.1.3.2 were used.

#### VI.2.1.3.2. Raman and fluorescence measurements obtained at GSI

For ruby the same scripts as described in section IV.2.2.2. was used to fit the double peak and calculate the pressure from the peak shift (Groß (2023)). The fitting range (692.5-698.0 nm) was adapted to the spectra depending on the background. A maximum uncertainty in pressure in the pressure range up to 6 GPa is estimated to be  $\pm 1.3\%$ , this is displayed in the error bars. The error of maximal  $\pm 0.086$  GPa was calculated by propagation of uncertainty. In some spectra, the 695 nm peak of samarium-strontium borate interfered with the ruby peak doublet. Therefore, I inserted a mask in the python script, to exclude the strontium peak during peak fitting of ruby peaks. The spectra with special fitting ranges and the ones with the masks are shown in table 12. The pressure was calculated using the formula

$$P[GPa] = 1.87(\pm 0.01) * 10^3 * \frac{\Delta\lambda}{\lambda_0} * [1 + 5.63(\pm 0.03) * \frac{\Delta\lambda}{\lambda_0}]$$
(8)

after the IPPS-Ruby2020 standard (G. Shen et al. (2020)). The measured R1 peak positions, at 694 nm, were inserted as  $\lambda$ -values.  $\Delta\lambda$  is the difference between the  $\lambda_0$  and measured (x) value at a certain pressure. For ruby the R1 peak at 694.23 nm (RbSr\_0000\_bar\_d\_000\_cV\_03 from 003\_PEB) was chosen as  $\lambda_0$ -value. This ambient position value is the same as that proposed by G. Shen et al. (2020). All spectra showed a relative error less than 0.03% for the fitted peak position. The FWHM of the fitted R1 peaks were less than 1.70 nm with a relative error <11%. For the peak fitting of strontium borate and calculation of the pressure from its peak shift, I modified another script based on the ruby one. The fitting range is 680-690 nm, except for the spectra listed in table 14. This script uses the formula

$$P[GPa] = 4.032 * \lambda_{0-0} * \left[\frac{(1+9.29 * 10^{-3} (\pm 4 * 10^{-4}) * \lambda_{0-0})}{1+2.32 * 10^{-3} (\pm 6 * 10^{-4}) * \lambda_{0-0}}\right]$$
(9)

for pressure calculation from the peak shift of strontium borate (Datchi et al., 1997). For the peak shift  $\Delta\lambda_{0-0}$ , the difference between the ambient pressure value at 684.42 nm (RbSr\_0000\_bar\_d\_000\_cV\_04 from 003\_PEB) and the measured peak position of the  ${}^{5}D_{0}$ - ${}^{7}F_{0}$  band were used. The ambient pressure value proposed by Datchi et al. (1997) is 684.41 nm. This difference of 0.01 nm compared to my measured peak position at ambient pressure corresponds to 0.04 GPa, far below the error value. All fitted spectra showed a relative error less than 0.02% for the fitted peak position. The FWHM of the fitted 0-0 peak was less than 0.34 nm with a relative error <0.6%. The quartz spectra were analyzed using a Python script (Groß (2023)). The pressure was calculated using the formula:

$$P[MPa] = 0.36079 * \Delta v^2 + 110.86 * \Delta v$$
(10)

where  $\Delta v$  is the difference between the reference ( $v_0 = 465.21 \text{ cm}^{-1}$  from Qzab\_0000\_bar\_d\_000\_cV\_01 from 003\_PEB) and current peak position ( $v_x$ ) of the 464 cm<sup>-1</sup> peak (Schmidt & Ziemann (2000)). The pressure calculated using Equation 10 has an uncertainty of ±50 MPa (Schmidt & Ziemann (2000)). For the pressure calculation from the 206 cm<sup>-1</sup> peak ( $v_0 = 206.00 \text{ cm}^{-1}$  from Qzab\_0000\_bar\_d\_000\_cV\_01 from 003\_PEB), the following formula was used (Schmidt & Ziemann (2000)):

$$P[MPa] = 0.4633 * \Delta v^2 + 31.66 * \Delta v$$
(11)

For the fitting of the quartz peaks, the intensities had to be rescaled between 0 and 100 a.u.. The linear trend lines were calculated by linear regression. The fitted peak position of samarium-doped strontium borate, ruby and quartz with their calculated pressure values are shown in table 15-23. The polynomial trend lines were calculated with NumPy, a package in the python script, which uses least squares method to fit the data (Harris et al. (2020)).

# VI.3. Development of gasket assembly for high temperature

The development of the gasket for high temperature was a successive process. In the time of development different kinds of materials were tested as gasket (see appendix table 24-26). The confining gasket material should be stiffer than the inner gasket material and should impede its intrusion. All tested gasket assembly were a stack of different materials to stabilize the oven and to guarantee insulation between the anvils. Instead of silver (Chapter IV) salt, NaCl (CAS:7647-14-5, Merck, Darmstadt), was used as second and inner gasket material. The sodium chloride added with about 10% water was prepressed using the prepressing jig with 90-100 bar/tn.

#### VI.3.1. Experiments with thermocouple

To assure a consistent and constant temperature inside the sample chamber, there has to be a measurement of the temperature of the sample volume. The first temperature measurements of inside the sample chamber were done with a K-type thermocouple. First thermocouple was sheathed with pyrophyllite (Figure 39, 4), the second and third were sheathed with an alumina sleeve (Degussit23; Friatec, Mannheim) (Figure 39, 9). A temperature controller (3204 and 3208, Eurotherm, Worthing, UK) displayed temperature values. All measurements were conducted with only one one-sided spherical diamond and the thermocouple inserted from above. For these experiments the axial channel of upper anvil was drilled to 5 mm (Figure 39c), to insert the thermocouple. The confining gasket was made of plastic, called PEEK 450g (melting temperature 616 K, tensile modulus at 296 K: 4000 MPa). This high-performance thermoplastic material is an unreinforced Polyether ether ketone (PEEK). Inner gasket was prepressed salt with a steel tube as oven. Angular graphite rings (Figure 39, 3) stacked on both ends of the steel heater connected the oven with the open tungsten carbide anvils. The one-sided spherical diamond was glued in the open tungsten carbide anvil.

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**Figure 39:** a) Salt gasket and pyrophyllite sheath (001\_PEA). b) PEEK-Salt gasket assembly after experiment (001\_PEA). c) Drawing of PEEK-Salt gasket assembly (002\_PEA and 003\_PEA). d) PEEK-Salt gasket assembly after experiment (002\_PEA). e) Open tungsten carbide anvil after experiment (001\_PEA). (1) Salt gasket, (2) steel oven, (3) graphite ring connections, (4) pyrophyllite sheath, (5) PEEK gasket, (6) open single-toroidal tungsten carbide anvil, (7) one-sided spherical diamond, (8) MgO, (9) alumina sheath. Yellow marking: shattered tungsten carbide anvil. Black bar indicates 5 mm.

The comparison of temperature measurements against the applied power of the heating system shows a high discrepancy between each experiment (Figure 40). In all experiments, the thermocouple broke in its length during the temperature measurements. The PEEK-salt gasket burst the tungsten carbide anvil after the first experiment (001\_PEA) (Figure 39e). During the increasing of the oil pressure from 60 bar to 125 bar, the thermocouple failed after reaching 595 K (322 °C). Probably at this time the outer rim of the tungsten carbide broke.



**Figure 40:** a) The applied voltage against the power output for experiments 001-003. b) Applied power against the measured temperature by means of thermocouple for experiment 001-003 PEA. The trend line for the 001 experiment  $T[K] = 0.0056 * P^2 - 0.8086 * P + 408.56$  with  $R^2 = 0.9845$  and trend line for the 003 experiment T[K] = 0.6726 \* P + 295.13 with  $R^2 = 0.9826$ .

In the first experiment (001\_PEA), the thermocouple failed after reaching 267 W and 595 K. After waiting for 5 min during voltage increase the current increased, hence the power. At 1.22 V the power increased by 3% (from 206 W to 212 W) (Figure 40a). At 1.30 V the power increased by 7% (from 248 W to 230 W). At 1.34 V the power increased by 3% (from 260 W to 267 W). The data demonstrate a stable voltage course, with the exception of the short circuit at 0.81 V, which resulted in a 49% reduction in power (from 95 W to 49 W). The temperature of the sample chamber exhibited a parabolic trend in accordance with the increase in power (Figure 40b). The second experiment (002\_PEA) experienced thermocouple failure immediately after the second voltage increase (Figure 40a). The thermocouple broke inside the sample chamber. In the third experiment, the achieved power was generally 80% lower compared to the initial experiments (Figure 40a). During the second measurement at 1 V, a power increase of 72% was observed. The oven ceased functioning at a voltage of 2.19 V, which was accompanied by an 87% reduction in power output, dropping from 273 W to 35 W. The temperature exhibited a linear increase with rising power (Figure 40b).


Figure 41: Position of thermocouple inside the sample chamber against temperature measurement.

In the experiment 003, the thermocouple was passed through the length of the sample chamber (Figure 41). The oven length was 3.0 mm. The lower part (about 0.5 mm) was filled with MgO (see Figure 39c). The length of the feed-through was 4.5 mm with 2 mm through the upper anvils. The upper part of the oven with length of 2.5 mm is displayed from 0.5-3.0 mm on the x-axis (Figure 41). At 3 W (corresponding to 297 K) the temperature fluctuates between 290 K and 291 K. Up to 18 W (corresponding to 307 K) the temperature was linearly distributed throughout the sample chamber. At 122 W (corresponding to 377 K) the highest temperature of 380 K (107 °C) was 1.7 mm after the diamond. 5 mm behind the diamond, 328 K (54 °C) was measured (49% less than the peak temperature). At 273 W (corresponding to 480 K) the peak temperature of 506 K (233 °C) in the sample chamber was at 2.4 mm. 4.6 mm behind the diamond, in the anvil channel, 413 K (140 °C) was measured (40% less than peak temperature). The peak temperature changed 0.7 mm towards the rim of the sample chamber. The peak temperature of the sample chamber shifted towards the upper anvil. Probably the lower diamond cooled the sample chamber from below.

# VI.3.2. Experiments with fluorescence measurements with glass window and PEEK gasket

The one-sided spherical diamond was replaced with a conical diamond with culet size of 1.2 mm and a table size of 1.3 mm (Type Ia – SOP25894, Böhler-Almax design 30°; Almax easyLab, Diksmuide, BE). The spherical diamond tended to slip inside the hemispherical indentation of the tungsten carbide anvil and forcing the salt irregular away, causing the anvil to break (Figure 39e). The tungsten carbide anvil with a conical indentation replaced one with a spherical recess. The conical diamond was glued in the conical indentation with a copper paste (245, OKS Specialty Lubricants Ltd., Maisach). Furthermore, a glass lens (Ø: 3.0 mm, 1.5 mm thick) was drilled with cooling water out of a microscope cover glass. This glass window was positioned behind the upper diamond, facing the Raman fiber (Figure 42b, 6). Samarium-doped strontium borate powder and synthetic ruby (1 mm irregular) was placed under the glass. In the process different kinds of stacked sample chamber filling were tested. The length of the oven has been adjusted several times to achieve homogeneous heating within the sample chamber. For the experiment 005 and ongoing, an Inconel tube was used as oven instead of steel. The dimension and angle of the bevel of the graphite rings had to be adjusted several times (see table 24-26), because graphite slipped inside the sample chamber (Figure 42d).



**Figure 42:** a) Photo of the PEEK-salt gasket before the experiment. b) Half-section drawing of the PEEK-salt gasket. c) Photo of experiment 004 with the oven encased in epoxy. d) Photo of experiment 005. e) Photo of experiment 006. (1) Open tungsten carbide anvil, (2) PEEK gasket, (3) salt, (4) graphite ring connection, (5) steel or Inconel oven, (6) glass window, (7) conical diamond, (8) ruby, and (9) samarium-doped strontium borate. Green arrow: direction of green laser, red marking: burnt salt caused by short-circuit. Black bar indicates 5 mm.

In all experiments with PEEK, the gasket flattened out and could not be pressurized above 380 bar oil pressure. The extrusion of plastic gasket caused a short circuit as the salt thinned between the anvils. The ovens with a length of 3.5 mm inflated (Figure 42c). The fourth experiment (004\_PEA) demonstrated a significant discrepancy in power output when the repeated set voltage was employed for higher values than 1 V (Figure 43a). The repeated measurement at 1.5 V shows an increase of 18% (from 203 W to 239 W). At a voltage of 2.0 V, there was a 24% increase in power output. For the highest set voltage of 2.5, the power output increased by 11% (from 713 W to 793 W). The fifth experiment shows the lowest voltage to output ratio of the peek-salt gaskets experiments. The third measurement at 2.0 V shows an increase in power of 27% (from 296 W to 376 W). The sixth experiment demonstrated a reliable voltage-to-power ratio, with nearly identical power outputs observed during repeated voltage increases and decreases. At 0.5 V, there was a 10% increase in power output for the first and third set voltages (from 30 W to 33 W). At a voltage of 1.5 V, there



was a 3% increase in power output (from 294 W to 302 W).

**Figure 43:** a) The applied voltage against the power output for experiments 004-006. b) Fluorescence spectra of 006 experiment at variable pressure.

The fluorescence spectra of the peek-salt gasket assemblies were partially successful (Figure 43b) with the majority of the spectra proving to be unanalyzable. For the 006 experiment, the 0-0 peak position of the samarium-doped strontium borate band at 3 bar was at 685.50 nm and shifted to 685.74 nm at 100 bar oil pressure. This peak shift of 0.24 nm corresponds to an increase in sample pressure of 0.96 GPa. At 3 bar, the ruby R1 peak position was at 694.45 nm, shifted to 694.90 nm. This peak shift of 0.45 nm corresponds to an increase in pressure of 1.22 GPa.

#### VI.3.3. Metallic gasket assembly with glass window

Due to the insufficient hardness of the PEEK gasket, subsequent experiments utilized a confining gasket composed of metal. In experiment 007, two muscovite sheets were stacked between two CuBe half-rings, following the configuration described in section V.2.1 (Figure 44a and b). The muscovite sheets experienced extrusion at a pressure of 60 bar. Nonetheless, the gasket maintained its insulating properties, as salt migrated between the CuBe half-rings.



**Figure 44:** a) Photo of CuBe-salt gasket assembly (007) during experiment. b) Photo of CuBe-salt gasket assembly (007) after experiment. c) Drawing of steel-salt gasket assembly (008). d) Photo of steel-salt gasket assembly (008) after experiment. (1) Plastic sleeve, (2) CuBe gasket, (3) muscovite, (4) salt, (5) graphite ring connection, (6) open tungsten carbide anvil, (7) conical diamond, (8) glass window, (9) ruby, (10) samarium-doped strontium borate and (11) steel gasket. Green arrow: direction of green laser. Black bar indicates 5 mm.

A gasket assembly comprising two steel rings and a single muscovite layer was also tested. However, the mica sheet extruded at approximately 190 bar, leading to an electrical short circuit. In experiments 008 and 009, silver pieces were implemented into the sample chamber to determine whether melting occurred. Since no evidence of melting was observed, the experimental temperature was inferred to be below 1235 K (962 °C) (Fischer et al. (1999)). To address the persistent issue of salt intrusion into the gasket assembly, a fired pyrophyllite ring was placed between the salt and the CuBe gasket (Figure 45). Additionally, a modified CuBe gasket design, based on Klotz et al. (2008), was incorporated. The detailed fabrication and implementation of the final CuBe-pyrophyllite-salt gasket are described in section VI.3.4. In experiment 010, a thermocouple was integrated into the assembly to monitor the temperature within the sample chamber (Figure 45c).



**Figure 45:** a) Photo of the gasket assembly before the experiment (009). b) Photo of the gasket assembly after the experiment (009). c) Drawing of the CuBe-pyrophyllite-salt gasket (010). d) Photo of the gasket assembly after the experiment (010). (1) Open tungsten carbide anvil, (2) conical diamond, (3) salt, (4) fired pyrophyllite, (5) CuBe gasket, (6) MgO, (7) Inconel oven, (8) graphite ring connection, (9) thermocouple, (10) glass window, (11) samarium-doped strontium borate, and (12) ruby. Green arrow: direction of green laser, red marking: crack in CuBe gasket. Black bar indicates 5 mm.

Post-experiment analysis revealed a rupture in the salt gasket and a visible crack in the CuBe gasket (Figure 45a, red circle). The voltage-to-power ratio exhibited a homogeneous parabolic trend across Experiments 007–010 (Figure 46a). In Experiment 009, the MgO spacer between the CuBe half-rings fractured at 1.0 V, resulting in a 52% increase in power output (from 61 W to 128 W). This instability in the outer gasket likely influenced the effective oven heating capacity. A smaller power increase of 3% was observed at 1.5 V (from 290 W to 299 W). Experiments 009 and 010 demonstrated nearly identical parabolic trends in the relationship between voltage and power output. The thermocouple temperature measurements followed a parabolic correlation with both the applied current and the power

supplied to the heating system (Figure 46b-d). The trend line

$$T[K] = 0.0017 * P^{2} + 1.1451 * P + 285.41$$
(12)

was utilized as the calibration curve for subsequent experiments, correlating the applied power to the sample temperature. The oven exhibited a uniform temperature increase at its central position without fluctuations, unlike those observed in earlier thermocouple experiments (see Figure 40).



Figure 46: a) Applied voltage against power output. b) Temperature measured with thermocouple against applied voltage. Trend line:  $T[K] = 284.19 * U^2 - 167.25 * U + 310.22$  with  $R^2 = 0.9965$ . c) Temperature measured with thermocouple against applied current. Trend line:  $T[K] = 0.0217 * I^2 - 1.3699 * I + 307.63$  with  $R^2 = 0.9981$  d) Temperature measured with thermocouple against applied power. Trend line:  $T[K] = 0.0017 * P^2 + 1.1451 * P + 285.41$  with  $R^2 = 0.9996$ .

Temperature measurements were conducted 20 seconds after each voltage increase, with a

second measurement taken after a 6-minute stabilization period. At 1.75 V, corresponding to 347 W (Figure 46b-d, green dot), the temperature rose from 875 K to 906 K (602-633 °C), representing a 5% increase. An IR thermometer was used to monitor the gasket temperature, which remained close to ambient conditions, ranging between 296 K and 300 K throughout the experiment.

In the fluorescence spectra, the ruby peak was not visible above 20 bar (Figure 47a). For experiment 010, the peak position of the samarium-doped strontium borate band at 20 bar was at 686.23 nm and shifted to 686.23 nm at 60 bar oil pressure (Figure 47b). This peak shift of 0.11 nm corresponds to an increase in sample pressure of 0.44 GPa.



**Figure 47:** a) Fluorescence spectra of experiment 010 at 20 bar (after Sakirzanovas et al. (2012)). b) Fluorescence spectra of experiment 010 at variable pressure and temperature.

#### VI.3.4. Final gasket design

At the Raman laboratory (GSI), three CuBe-pyrophyllite-salt gasket assemblies were prepared for fluorescence and Raman measurements. The final gasket-sample chamber design was implemented in two configurations: one assembly incorporating a glass window and another without a glass window. The following section provides a detailed description and evaluation of both designs.

#### VI.3.4.1. CuBe-pyrophyllite-NaCl gasket with glass window

The final gasket for the HT-D-PEC was a stack of three materials, from the outermost copperberyllium, pyrophyllite and salt. Two copper-beryllium half rings were glued together with a layer of magnesium oxide (0.3 mm thick). First the MgO was ground in an agate mortar to a very fine powder, then mixed with distilled water till it had a honey-like texture (private communication, Dr. Stefan Klotz). Out of a pyrophyllite rod was turned a square-edged ring on a lathe machine (OD: 9.8 mm, ID: 7.0 mm, height: 1.8 mm). The pyrophyllite ring was fired at 1223 K for 3 h. On the gasket mounting jig the two copper-beryllium halves were glued together with the MgO glue. With a razor blade the excess glue was pressed out to the sides and removed. Then the fired pyrophyllite ring was inserted and glued in.

Salt was the innermost gasket material. The NaCl was crushed in a mixer to fine powder. With an agate mortar, 0.395 g dry salt was mixed with distilled water (10%). The first half of the powder was inserted in the prepressing jig. Then a steel ring was inserted in the prepressing jig to reduce its diameter to 7.0 mm and the second half of powder was poured in. The mixture was pressed with 90-100 bar/tn for 3 min. The salt was shaped into a bicone ( $\emptyset$ : 7.00 mm, h 5.6 mm center, height 2.0 mm at the edge). Then the salt bicone was drilled with aid of a drilling jig. The drilling jig had several inserts to secure the salt. The drilling jig had to be clamped under an electric drill. First the salt bicone was drilled with a 1.0 mm boring head, then the boring head were successively increased to 2.0 mm and 3.6 mm, as well as the inserts of the drilling jigs. Finally, the NaCl had a 3.7 mm centered hole. The surface of the drilled hole was manually ground to be smooth. Then the edges of the drilled hole were ground manually with sand paper to a height of 4 mm (NaCl: OD: 7.00 mm, ID: 3.7 mm, height: 4.0 mm in the center, height: 2.0 mm at the edge).

The sample chamber was also stacked. The sample and the pressure transmitting media were stacked inside the oven, before the oven was inserted in the CuBe-pyrophyllite-NaCl gasket. The oven was shortened with a diamond blade saw out of an Inconel pipe (OD: 3.7 mm, ID: 3.5 mm, height: 5.5 mm). The sample chamber consisted of prepressed salt. About 0.1 g NaCl was fine ground and added with distilled water (10%). With aid of the sample chamber jig and a hand press the sample chamber was filled. First about a spatula tip of salt was filled to height of 1 mm in the oven and prepressed. Prepressing was done hand-tight with a dornpress (Typ WP-Junior, Weidmann, Rapperswil-Jona, CH). On one side strontium borate and on the other side a small synthetic ruby crystal (1 mm irregular fragment) was placed. This was covered with salt (1 mm in height) and again pressed. For the experiment 002 PEB, a glass window was inserted and at the edges and on top covered with salt (Figure 48a). Then the sample, in this case a quartz lens drilled out of a single crystal (OD: 2.0 mm, height: 2.0 mm; Valmalenco, IT) was inserted. The edges were filled with salt and the height of the oven was filled with salt and pressed hand-tight. This sample chamber-oven assembly was stacked into the salt bicone. The salt bicone was then stacked into the CuBe-pyrophyllite gasket.

Two graphite ring connections connected the Inconel furnace to the open tungsten carbide anvils. The graphite rings (OD: 4.0 mm, ID: 3.8 mm, height: 0.8 mm) with outwardly beveled edges and a wedge-shaped half section were turned on a lathe from a graphite bar. Excess edges were sanded to a smooth surface. Both rings are stacked over the edges of the furnace, one at the bottom and one at the top. The gasket-sample chamber assembly was then placed on the open single-toroidal anvils. Before the gasket assembly was positioned, the diamond window was glued into the conical recess of the anvils using three dots of high temperature copper adhesive applied to the conical surfaces of the diamond.



**Figure 48:** a) Drawing of the CuBe-pyrophyllite-salt gasket with glass window (002\_PEB) b) Photo of the CuBe-pyrophyllite-salt gasket with glass window (002\_PEB) after experiment. (1) Open tungsten carbide anvil, (2) conical diamond, (3) salt, (4) pyrophyllite, (5) CuBe gasket, (6) MgO, (7) Inconel oven, (8) graphite ring connection, (9) samarium-doped strontium borate, (10) ruby, (11) glass window, (12) quartz, (13) plastic sleeve, and (14) connection to water cooling system. Black bar indicates 5 mm.

### VI.3.4.2. CuBe-pyrophyllite-NaCl gasket without glass window

Experiments 003\_PEB and 004\_PEB were conducted without a glass window. The CuBepyrophyllite-NaCl gasket assembly, excluding the glass window, was prepared according to the same protocol as the assembly with a glass window. Approximately 0.1 g of NaCl was finely ground and mixed with distilled water (10% by weight). A thin layer of salt (1 mm in height) was placed inside the oven and compacted. On one side of the assembly, strontium borate was positioned, while a small synthetic ruby crystal (an irregular fragment of 1 mm in size) was placed on the opposite side (Figure 49a). This setup was covered with an additional 1 mm layer of salt and compressed again. A quartz lens (Ø: 2.0 mm; height: 2.0 mm; Valmalenco, Italy) was inserted into the assembly, and the edges were filled with salt. The remaining volume of the oven was also packed with salt and compressed by hand. During Experiment 004\_PEB, a short circuit occurred after reaching a pressure of 112 bar. Two minutes later, at the same pressure, a loud "klack" noise was observed, accompanied by an overflow of current. This short circuit was visible in form of molten graphite (Figure 49b).



**Figure 49:** a) Drawing of the CuBe-pyrophyllite-salt gasket without glass window b) Photo of the CuBe-pyrophyllite-salt gasket without glass window after experiment (003\_PEB) c) Photo of the CuBe-pyrophyllite-salt gasket without glass window (004\_PEB) after experiment. (1) Open tungsten carbide anvil, (2) conical diamond, (3) salt, (4) pyrophyllite, (5) CuBe gasket, (6) MgO, (7) Inconel oven, (8) graphite ring connection, (9) samarium-doped strontium borate, (10) ruby and (11) quartz. Black bar indicates 5 mm.

# VI.4. Results

## VI.4.1. Cube-pyrophyllite-NaCl gasket assembly with glass window

In the 002\_PEB experiment, the pressure was gradually increased from 14 bar to 40 bar and then to 60 bar over a period of 5 hours. During the heating process, the applied voltage was incrementally increased from 0 V to 1.00 V in steps of 0.25 V, with each step lasting 5 minutes. During this time, the oil pressure displayed fluctuations between 60 and 61 bar. Fluorescence measurements were successfully performed from the beginning of the experiment using 30 mW of laser power. On the second day of the experiment, a short circuit occurred at a pressure of 135 bar and a current of 350 A. Following the short circuit, the gasket assembly was subjected to a pressure test up to 600 bar, with pressure releases recorded every 4–5 minutes. Raman peaks of quartz were not detectable throughout the experiment. However, fluorescence measurements continued to be successful. Post-experiment analysis revealed that the gasket assembly remained intact and displayed symmetric deformation (Figure 48b).

#### VI.4.1.1. Samarium-doped strontium borate results

The measured oil pump pressure (in bar) was consistent with the calculated sample chamber pressure (in GPa) derived from the peak shift of samarium-doped strontium borate (Figure

50). The largest discrepancy was observed between an oil pressure of 466 bar, corresponding to a peak shift of 1.48 nm (5.86 GPa), and 480 bar, corresponding to a peak shift of 1.50 nm (5.93 GPa). The maximum oil pressure reached during the pressurization phase was 600 bar, which resulted in a sample chamber pressure of 6.71 GPa and a peak shift of 1.70 nm. After a 30-minute hold, the oil pressure decreased to 593 bar, while the measured peak shift increased. During the pressure release phase, at 593 bar, a peak shift of 1.84 nm was observed, corresponding to a pressure of 7.20 GPa. Following a five-minute interval after reaching a certain oil pressure, a second measurement of the fluorescence signal was conducted. Over the five-minute observation period, the oil pressure exhibited a maximal decrease of 8 bar, while the calculated pressure demonstrated a maximal increase of 0.08 bar. The observed 8 bar pressure reading is approximately three times greater than the calculated error associated with the oil pressure pump. The pressure release path exhibited a slight parabolic trend.



**Figure 50:** Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the strontium borate peak at 685 nm (at 298 K) (Datchi et al. (1997)). Light points represent the increasing pressure. Dark symbols represent decreasing pressure path. Trend line is  $P[GPa] = 0.0102 * P_{oil} + 0.7642$  with  $R^2 = 0.9571$ . For the peak shift the trend line is  $\lambda[nm] = 0.0026 * P_{oil} + 0.783$  with  $R^2 = 0.9573$ .

During isobaric heating at 60 bar, with the voltage increasing from 0 V to 1 V, the 0-0 peak of samarium-doped strontium borate shifted from 685.73 nm to 685.76 nm (Figure 51a). This shift of 0.03 nm corresponds to a pressure change of 0.12 GPa, which is negligible. The intensity of the peak decreased by only 6%, from 7118 a.u. to 6662 a.u..



**Figure 51:** a) Fluorescence spectra of the 0-0 peak position (in nm) of the samarium-doped strontium borate with increasing voltage from 0 to 1 V. b) Fluorescence spectra of the 0-0 peak position (in nm) of the samarium-doped strontium borate with increasing waiting time before measurement at 60 bar and 1 V.

At 61 bar and 1 V, the 0-0 peak was measured after 1 min, 4 min, 7 min and 10 min at the same spot (Figure 51b). During 10 min the peak shifted 0.02 nm (from 685.74 nm to 685.76 nm) corresponding to 0.08 GPa. The intensity increased for the later measurements from 6662 to 7890 a.u., a rise of 18%.

#### VI.4.1.2. Ruby results

The measured oil pump pressure (in bar) was consistent with the calculated pressure (in GPa) assumed within the sample chamber (Figure 52). Above 409 bar, the ruby peaks became undetectable and remained so throughout the pressure release phase. This may have been due to the deformation of the sample chamber, which likely caused an excessive accumulation of salt and samarium-doped strontium borate around the ruby, obscuring its signal. At 409 bar, the ruby peak shifted by 1.31 nm, corresponding to a pressure of 3.57 GPa.



**Figure 52:** Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the ruby at 694 nm (at 298 K)(G. Shen et al. (2020)). Trend line is  $P[GPa] = 0.0066 * P_{oil} + 0.6851$  with  $R^2 = 0.9980$ . For the peak shift the trend line is  $\lambda[nm] = 0.0024 * P_{oil} + 0.2578$  with  $R^2 = 0.9979$ .

Figure 53a provides a detailed view of the peak shift during isobaric heating. The ruby peaks shifted by 0.47 nm, resulting in a calculated pressure of 1.27 GPa. At 1 V the double peak broadened significantly. Furthermore, the intensity of the R1 peak decreased by 66%, from 6132 a.u. to 2096 a.u., as the temperature increased. For the measurement at the same location over a 10-minute period, the R1 peak remained stable (Figure 53b). Compared to the initial measurement, the intensity increased by approximately 48%, from 2069 a.u. to 3069 a.u.. The peak shift of 0.01 nm, corresponding to a pressure change of 0.03 GPa, is considered negligible.



**Figure 53:** a) Fluorescence spectra of the peak position of the R1 and R2 band (in nm) of ruby with increasing voltage from 0 to 1 V. b) Fluorescence spectra of the peak position of the R1 and R2 band (in nm) of the ruby with increasing measurement time at 60 bar and 1 V.

#### VI.4.2. Cube-pyrophyllite-NaCl gasket assembly without glass window

All measurements were performed at 25 mW laser power.

#### VI.4.2.1. Samarium-doped strontium borate results

As ambient pressure condition, a pressure of 0 bar on the pressure release path was set with a peak position at 685.42 nm. The second fluorescence measurement of strontium borate at 20 bar was conducted 2 hours and 30 minutes after the first measurement, and it showed the same peak position. This suggests that the sample chamber likely relaxed during this time, with no overpressure present, as observed in the initial measurement at 20 bar. The diagram of oil pressure against the peak shift of strontium borate shows a parabolic trend (Figure 54). At maximum reached oil pressure with 599 bar a peak shift of 0.91 nm was measured, which corresponds to the calculated sample pressure of 3.63 GPa. At 0 bar the measured peak shift is 0.05 nm corresponding to 0.20 GPa.



**Figure 54:** Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the samarium-doped strontium borate peak at 685 nm (at 298 K) (Datchi et al. (1997)). Light points represent the increasing pressure. Dark symbols represent decreasing pressure path. The trend line is  $P[GPa] = 1.462 * 10^{-8} * P_{oil}^3 - 2.487 * 10^{-6} * P_{oil}^2 + 0.001038 * P_{oil} + 0.8146$  with  $R^2 = 0.9970$ . For the peak shift the trend line is  $\lambda[nm] = 3.547 * 10^{-9} * P_{oil}^3 - 4.279 * 10^{-7} * P_{oil}^2 + 0.0001686 * P_{oil} + 0.2146$  with  $R^2 = 0.9967$ 

During heating at 60 bar, with the voltage increasing from 0 V to 1.70 V, the 685.5 nm peak shifted to 685.65 nm, a change of only 0.15 nm. This peak shift corresponds to a pressure increase of 0.60 GPa. During the isobaric heating (experiment 003\_PEB) at 60 bar the 0-0 peak of samarium-doped strontium borate experienced an immense decrease in intensity of about 97% (from 20547 to 644 a.u.) (Figure 55). At 1.3 V (202 W and corresponding 585 K), the 0-0 peak became difficult to distinguish. Above 1.5 V, 279 W and 737 K, the peak was not measurable. The shift of 0.10 nm corresponds to a pressure rise of 0.40 GPa.



Figure 55: Fluorescence spectra of the 0-0 peak position (in nm) of the strontium borate with increasing voltage from 0 to 1.5 V at 60 bar.

In the first heating steps up to 1 V the oil pressure fluctuates between 59 and 60 bar. Above 1.3 V the oil pressure increased from 61 to 64 bar for 1.7 V.

#### VI.4.2.2. Ruby results

The peak shift and corresponding calculated pressure against the set oil pressure exhibits a parabolic trend with

$$P[GPa] = 6.034 * 10^{-10} * P_{oil}^3 + 1.245 * 10^{-5} * P_{oil}^2 - 0.00329 * P_{oil} + 1.136$$
(13)

with  $R^2 = 0.9975$  (Figure 56). The measurement at 0 bar was set as ambient peak position for the R1 peak. At 599 bar the R1 peak at 695.6 nm (shifted 1.37 nm) indicating a sample pressure of 3.73 GPa. This is 0.10 GPa higher than the calculated pressure for samariumdoped strontium borate. At 0 bar a peak shift of 0.08 nm was measured, which corresponds to a sample pressure of 0.22 GPa.



**Figure 56:** Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the ruby at 694 nm (at 298 K)(G. Shen et al. (2020)). The trend line is  $P[GPa] = 6.034 * 10^{-10} * P_{oil}^3 + 1.245 * 10^{-5} * P_{oil}^2 - 0.00329 * P_{oil} + 1.136$  with  $R^2 = 0.9975$ . For the peak shift the trend line is  $\lambda[nm] = 7.862 * 10^{-11} * P_{oil}^3 + 4.685 * 10^{-6} * P_{oil}^2 - 0.001232 * P_{oil} + 0.4215$  with  $R^2 = 0.9975$ 

During isobaric heating at a constant pressure of 60 bar, the R1 peak exhibited a shift of 0.53 nm, corresponding to a calculated pressure increase of 1.43 GPa. Additionally, the intensity of the R1 peak exhibited a notable decline, decreasing by 82% from 12056 a.u. to 2212 a.u. across the voltage range from 0 V to 1.3 V (Figure 57). At voltages exceeding 1.3 V (equivalent to 202 W and an assumed temperature of 584 K), the ruby fluorescence peaks became indistinguishable.



Figure 57: Fluorescence spectra of the peak position of the R1 and R2 bands (in nm) of the ruby with increasing voltage from 0 V to 1.3 V at 60 bar.

#### VI.4.2.3. Quartz results

Raman measurements of quartz were successfully conducted at the 206 cm<sup>-1</sup> and 464 cm<sup>-1</sup> peaks for the experiment 003\_PEB. The quartz signal remained detectable up to a pressure of 65 bar and a voltage of 1.8 V (Figure 59). The 206 cm<sup>-1</sup> peak was undetectable at the experiment 004\_PEB. For the pressure calibration (experiment 003\_PEB), the quartz peak shift and calculated pressure against the set oil pressure exhibits a parabolic trend. At 603 bar the peak position was at 491.9 cm<sup>-1</sup>, shifted 26 cm<sup>-1</sup>, indicating a sample pressure of 3.22 GPa (Figure 58). This is 0.51 GPa lower than the sample pressure calculated for ruby.



**Figure 58:** Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the quartz at 464 cm<sup>-1</sup> (at 298 K) (Schmidt & Ziemann (2000)). The trend line is  $P[GPa] = 2.104 * 10^{-8} * P_{oil}^3 - 1.361 * 10^{-5} * P_{oil}^2 + 0.005401 * P_{oil} + 0.3666$  with  $R^2 = 0.9885$ . For the peak shift the trend line is  $\nu[cm^{-1}] = 1.614 * 10^{-7} * P_{oil}^3 - 1.044 * 10^{-4} * P_{oil}^2 + 0.04372 * P_{oil} + 3.509$  with  $R^2 = 0.9880$ .

The calculated sample pressures out of the peak shift of both peak positions resulted in 0.34 GPa (for 206 cm<sup>-1</sup> band) and 0.35 GPa (for 464 cm<sup>-1</sup> band) at 60 bar oil pressure during isobaric heating. This is a hypothetical sample pressure. In general, the 206 cm<sup>-1</sup> was less prominent than the 464 cm<sup>-1</sup>, yet both exhibited analogous trends (Figure 59). For the 206 cm<sup>-1</sup> peak as well as for the 464 cm<sup>-1</sup> peak, their position unheated (at 0 V) and their position at maximum temperature (1.80 V corresponding to 405 W), approximately 1028 K is nearly the same (Figure 59). The Raman shift of 0.06 cm<sup>-1</sup> to lower wavenumbers (from 468.27 to 468.33 cm<sup>-1</sup>) during isobaric heating, corresponds to a pressure decrease of 0.01 GPa. However, after the first voltage increase (to 0.6 V corresponding to 336 K (63 °C)) the 464 cm<sup>-1</sup> peak wanders to 471.31 cm<sup>-1</sup>. The peaks initially exhibited a shift towards higher wavenumbers up to 1 V, and subsequently towards lower wavenumbers above 1.2 V. The intensity of the peak increased (3152 a.u.), as the background increased (from 500 to 2000 a.u.). At 0 V, and the peak at 215.48 cm<sup>-1</sup> has an intensity of 890 a.u., which increases by 8% compared to the peak position at 1.8 V (with 964 a.u.).



**Figure 59:** a) Raman spectra of the peak position of the 206 cm<sup>-1</sup> of the quartz with increasing voltage at 60 bar for experiment 003\_PEB. b) Raman spectra of the peak position of the 464 cm<sup>-1</sup> of the quartz with increasing voltage at 60 bar for experiment 003\_PEB

#### VI.5. Discussion

The development of a high-temperature gasket with two diamond windows was an iterative process. Throughout this process, several adjustments were required the choice of materials and their dimensions to optimize the design.

#### VI.5.1. Development of the HT gasket assembly

The gasket assembly was refined through a process of trial and error. Early prototypes incorporating a plastic ring as a confining gasket failed to withstand the applied pressures. Experiments 001–006 were conducted up to a maximum of 380 bar and 546 W, but the oven exhibited poor power distribution. The steel oven experiments demonstrated a higher degree of inconsistency in comparison to the experiments conducted with an integrated Inconel oven. During the experiment with thermocouples, it was observed that the temperatures achieved were approximately one-third lower in the case of the steel oven (Figure 60a). The initial three experiments showed considerable variability in power output. In particular, the third experiment produced power outputs that were, on average, 80% lower than those observed in the first two experiments. This discrepancy is likely attributable to the shorter length of the steel oven, which measured only 3 mm in these trials. In comparison, the sixth experiment with an Inconel oven, conducted with an oven length of 4.7 mm and with repeated voltage cycles, exhibited a more stable and reliable power output (Figure 60b).



**Figure 60:** a) Applied power against the measured sample temperature with a thermocouple. b) Applied voltage against the power of the heating system of the HT-D-PEC. Black: steel oven; colored: Inconel oven.

The material composition and length of the oven significantly influenced the voltage-to-power output ratio. Experiments using steel ovens exhibited a wider variation in this ratio, while the oven length affected the repeatability of the measurements. In contrast, experiments with Inconel ovens demonstrated greater consistency and repeatability in power output at a given voltage. In general, the fluorescence measurements of ruby and samarium-doped strontium borate were successful. However, the ruby signal could not be interpreted to calculate the sample pressure because the resolution of the spectrometer is too poor for the high temperature experiments. For the experiment 010, at 60 bar oil pressure, the sample pressure was 3.15 GPa, calculated from the samarium-doped strontium borate peak shift (0.79 nm). This is more than twice as high as in the following experiments. Probably, the ceramic from the thermocouple filled the sample chamber and made it stiffer. Therefore, the salt and the pressure gauges could be pressurized more efficiently than in a salt-only chamber.

#### VI.5.2. Comparison of the gasket assembly with and without glass window

The final gasket assemblies with and without a glass window reproduced the power and temperature ratios of the 010 experiment. The applied voltage to power ratio is well in accordance with the thermocouple experiment (Figure 61a). The applied power of the CuBe-pyrophyllite-NaCl gasket experiment was maximal 9% higher than 010 experiment, whereas the applied power of the assembly with glass window was maximal 12% lower. Probably the glass window had a cooling effect, due to the higher heat conductivity of glass

than salt. The trend line calculated out of experiment 010 measured temperatures is well aligned with the calculated sample chamber temperatures for the final gaskets (Figure 61b). The calculated temperature of the CuBe-pyrophyllite-NaCl gasket experiment was maximal 11% higher than the trend line.

The sample pressure was calculated from the peak shift of samarium-doped strontium borate and compared with those of ruby and quartz. Ruby served as the standard pressure gauge for the in-situ HP-HT experiments. However, the ruby double peaks broaden to an asymmetrical band, making a pressure determination more unreliable with higher temperature (Datchi et al. (2007)). In addition, the signal-to-noise ratio of the ruby doublet decreases, making the R1 peak almost undetectable above 700 K (427 °C) (Datchi et al. (1997)) (Figure 53a and 57). An uncertainty of 5 K on temperature leads to an uncertainty of about 0.1 GPa on pressure while determination of pressure via ruby peak shift (Datchi et al. (1997)). The fluorescence signal of samarium-doped strontium borate (SrB<sub>4</sub>O<sub>7</sub>:Sm<sup>2+</sup>) was measured to ascertain pressure. The  $SrB_4O_7$ :  $Sm^{2+}$  was synthesized by Datchi et al. (1997 and 2007). The strontium borate is stable from 0-86 GPa and 900 K (627 °C) (Datchi et al. (2007)). The 0-0 fluorescence line (also called  ${}^{7}D_{0}{}^{-5}F_{0}$ ) is a very narrow line (1.5 ÅFWHM) at 685.41 nm (Lacam & Chateau (1989)). Compared to ruby, non-hydrostaticity has a lesser effect on the wavelength shift and intensity of the fluorescence line (Datchi et al. (1997)). Its temperature shift is negligible, with only minor thermal broadening of the peak (Datchi et al. (1997)). This was also observed in the heating experiment of this study (Figure 55). The peak shift of 0.40 GPa was measured at 737 K (464 °C). Nevertheless, it has a rapid decrease of fluorescence intensity above 500 K (Datchi et al. (2007)). The decrease of intensity of the fluorescence signal occurred at 42 W (0.6 V), resulting in 336 K (63 °C). Measuring the peak shift in the Raman signal of quartz allows for the calculation of the pressure exerted on the mineral after Schmidt et al. (2000). These three spectroscopic pressure gauges were used in a first attempt to calibrate the CuBe-Pyrophyllite-NaCl gasket assembly.

The comparison of waiting time between measurement periods showed no essential changing of the fluorescence peak position during the heating of the sample chamber. This samarium-doped strontium borate peak shift of 0.02 nm (which is a calculated sample pressure of 0.08 GPa) during 10 minutes is negligible and can be seen as an error in peak fitting (Figure 51b). Longer waiting times between measurements only increased the peak intensity by 18%. The same is true for the ruby peak shift of by 0.01 nm, which corresponds to 0.03 GPa (Figure 53b). However, the ruby band intensity increased about 48% after 10 minutes. This makes samarium-doped strontium borate a more reliable pressure gauge.

Both gasket assemblies showed a decrease of intensities of the fluorescence peaks during heating. The gasket without window showed an intensity decrease of 97%, whereas the gasket with glass window showed only a decrease of 6% (Figure 51a and 53a). Maybe the salt in the gasket without window experienced a structural change, which degrades the fluorescence signal.

The final gaskets exhibit different behavior with regard to pressure generation within the sample chamber (Figure 61c). In the case of the gasket assembly with a glass window, the calculated pressures of ruby and samarium-doped strontium borate diverge. At 409 bar, the strontium borate pressure (at 5.31 GPa) is 1.96 GPa higher than the ruby pressure (at 3.35 GPa), representing a discrepancy of 37%. One source of experimental error was the pressure and temperature gradients within the sample chamber. This problem was addressed by positioning the two fluorescence instruments close together to minimize measurement discrepancies. However, the glass window experiment required repositioning of the spectroscopic setup. During heating (at 48 bar), the long-distance microscope had to be adjusted by 2.8 mm in the horizontal axis and 3 mm in the depth plane. This is an indication that the ruby could be repositioned to the edge of the sample chamber and therefore experienced lower pressures. In the sample chamber the pressure distribution is probably heterogeneous, and higher pressure are expected in the center.

The calculated pressures for strontium borate, ruby and quartz in the gasket assembly without glass window are well aligned (Figure 61d). Ruby and quartz show nearly the same pressure, as both were positioned in the center of the sample chamber. The slightly lower pressure for strontium borate is to be expected, as it is positioned near the rim of the sample chamber.

The main drawback of the gasket assembly with a glass window is that no Raman measurement succeeded. Probably the glass diminished the Raman signal of quartz. In addition, the integration time of the fluorescence measurement with glass window was two to three times longer (see appendix table 27 and 28). The sample chamber with glass window reached twice as high pressures as the sample chamber without a window (Figure 61e). At 600 bar the sample chamber with a glass window reached 7.2 GPa, whereas the sample chamber without succeeded only 3.63 GPa. Moreover, the assumed sample pressure for the sample chamber with a glass window demonstrates a linear trend, whereas the sample chamber with only salt exhibits a parabolic trend. A possible reason could be the lower compressibility of the glass window compared to the salt. When pressure is applied, the volume of the sample chamber is reduced and the pressure is more effectively distributed towards the sample.

In chapter IV, a gasket comprising steel and silver was employed for the purpose of pressure calibration at ambient temperature. A comparison of the high-temperature gaskets with the gasket used at ambient temperature indicates that the ambient temperature gasket yields intermediate performance results between the two HT designs (Figure 61f). The ambient temperature gasket and the high-temperature gasket with a glass window exhibit a linear correlation between oil pressure and sample pressure.



**Figure 61:** a) Applied voltage against power output. b) Calculated temperature against applied voltage. Trend line of experiment 010:  $T[K] = 284.19 * U^2 - 167.25 * U + 310.22$ . c) Diagram of the measured oil pressure (in bar) against the calculated pressure (GPa) for the gasket assembly with glass window. d) Diagram of the measured oil pressure (in bar) against the calculated pressure (in bar) against the calculated pressure (GPa) for the gasket assembly without glass window. e) Comparison of measured oil pressure (in bar) against the calculated pressure (GPa) after the peak shift of the strontium borate peak. f) Diagram of the measured oil pressure (in bar) against the calculated pressure (in bar) against the calculated pressure (GPa) out of the ruby peak shift for the high temperature (HT) gaskets and the ambient temperature (RT) gasket.

## VI.5.3. Quartz transition

During isobaric heating with the gasket assembly without glass window, the  $\alpha$ - $\beta$  quartz transition could probably be observed. At 60 bar oil pressure the calculated pressure from the peak shift were 0.32 GPa for strontium borate, 0.27 GPa for ruby and 0.35 GPa for quartz. A. Shen et al. (1993) calculated the  $\alpha$ - $\beta$  quartz transition temperature with following equation:

$$T[^{\circ}C] = 574.3 + 0.2559 * P - 6.406 * 10^{-6} * P^{2}[MPa]$$
(14)

Using this equation, the  $\alpha$ - $\beta$  quartz transition temperature at 0.27-0.35 GPa is 916-936 K (643-664 °C). During isobaric heating at 60 bar, the Raman bands, 206 cm<sup>-1</sup> and 464 cm<sup>-1</sup> respectively, wandered first to higher and then to lower wavenumbers. The 206 cm<sup>-1</sup> band broadened above 0.5 V and could not be fitted. Above 237 W (1.4 V), corresponding to 652 K, the 355 cm<sup>-1</sup> mode from  $\alpha$ -quartz disappeared (Schmidt & Ziemann (2000)) (Figure 62). The appearance of the 244 cm<sup>-1</sup> line, an indication for  $\beta$ -quartz, could not be observed.



Figure 62: Raman spectra of quartz (in  $cm^{-1}$ ) with increasing voltage.

A comparison was made between the data of this study and that of Schmidt et al. (2000). The temperature was calculated from the trend line of experiment 010 using the power output. The frequency shifts of the 464  $\text{cm}^{-1}$  quartz band showed similar trend to that of

Schmidt et al. (2000), but at higher values. The isobar slope  $-0.014 \text{ cm}^{-1}/\text{K}$  determined by Sharma (1989), Gillet et al. (1990) and Castex & Madon (1995) is well aligned with the obtained data from 336-651 K (63-378 °C). But the calculated quartz transition at 916-936 K (643-664 °C) is about 100 K above the frequency shift change around 737-819 K (464-546 °C) (Figure 63a).



**Figure 63:** a). Frequency shift with temperature of the 464 cm<sup>-1</sup> Raman band of quartz. b) Linewidth (FWHM) of the 464 cm<sup>-1</sup> Raman band of quartz with increasing temperature.

# VII. Swift heavy ion irradiation experiments

The D-PEC with axial channel also works as an irradiation access at ion accelerator facilities (such as GSI, Darmstadt). This way it is possible to obtain pressure and temperature data by measuring the shift of Raman bands or fluorescence lines of the standard material, quasi-simultaneously or shortly after the ion irradiation.



**Figure 64:** Experimental setup in cave A at GSI, Darmstadt. (1) HT-D-PEC, (2) long-distance microscope, (3) SuperHead, (4) reference heater and (5) ion beam.

In April 2019, the HT-D-PEC was tested in the high-energy experimental hall, Cave A at GSI, Darmstadt, for the first time under these conditions. For the first time the D-PEC with both diamond windows and the HT gasket assembly made of NaCl and CuBe was irradiated (as described in section V.2.). The HT-D-PEC heated the quartz and apatite samples at 473 K. The irradiation was performed in cave A at the SIS18 using a focused beam of Ag ions of 270 MeV/n initial energy. The silver ions with a fluence of  $2 \times 10^{11} \text{ ions/cm}^2$  passing through secondary electron transmission monitor (Ti), the aluminium window, an air gap, the diamond window, water (the PTM), and finally deposit in the apatite and quartz mineral (Figure 65). The energy loss of silver ions passing through these materials, was calculated with SRIM (see table 4). Generally, an error of 15% uncertainty is attributed to the calculation code (Ziegler et al. (2010); Wittmaack (2016)).



Figure 65: Schematic of the experimental setup. (not to scale)

The table 4 shows the energy loss of an Ag ion as a function of its kinetic energy. The first test irradiation of the modified HT-D-PEC was conducted at the GSI, Darmstadt. The in-situ measurements were carried out with the HT gasket (as described in section V.2.).

material	thickness [mm]	$E_{in}$ [MeV/u]	$E_{out}$ [MeV/u]
detector (Ti)	0.03	270	269
window (Al)	0.10	269	268
air gap	450.00	268	264
diamond	1.50	264	225
water <sub>liquid</sub>	2.00	225	207
quartz SiO $_2$	2.00	207	168
apatite $Ca_5P_3O_{12}F_1$	2.00	168	108

 Table 4: Energy deposition in apatite inserted in the HT-D-PEC calculated with SRIM.

Due to construction faults, the brass jacket could so far only be used on one side and thus not for cooling, but only as a connection to the resistance heating (as described in Section V.2.5.). The CuBe-NaCl gasket was mounted in the anvils. The sample chamber was filled with distilled water as pressure transmitting medium and quartz and apatite as sample. The quartz was positioned with its c-axis parallel to the ion beam. The apatite was placed with its c-axis perpendicular to the ion beam. The oil pressure was set to 25 bar, which corresponds to about 1.5 kbar (0.15 GPa). Under elevated pressure and temperature conditions (about 473 K), the natural minerals were bombarded with swift heavy ions such as <sup>107</sup>Ag. The apatite and quartz in the HT-D-PEC was under pressure for 4 months, as the press frame

became ion-induced activated. As a reference, a second sample of apatite was penetrated at 473 K and atmospheric pressure in a custom-built ceramic heater (Figure 64). The oven is heated by a high temperature bar heater (8786M8XX; Paul Rauschert GmbH, Scheßlitz) made of  $Al_2O_3$  ceramics. A brass screw behind the resistance heater held the sample. The ceramic oven was mounted in front of the HT-D-PEC in beamline and was removed after irradiation. The samples were heated for about 2 h.

The spectroscopic analysis system tested in the GSI beam time (Figure 64) was the same as described in Section IV.2.2.1.2.). The SuperHead was attached to an adjustable stage to ensure that the laser beam was focused on the sample. The attempt of an in-situ measurement failed due to high fluctuations caused by high ion and neutron activation scattering onto the spectrometer. This in-situ HT-D-PEC was successfully tested in cave A in the GSI beam time (April 2019), but did not yield usable measurement values. In the future, it is important that the spectrometer is encased or positioned outside of Cave A, because inside the scattered ions interfered and completely overlaid the measured signals.

Ex-situ Raman measurements were conducted utilizing the Raman setup at Heidelberg University (see Section IV.2.2.1.2.). All measurements were performed with an objective lens of 20x magnification and a laser power setting of 90 mW. Each measurement location was repeatedly measured for 20 seconds twice.



**Figure 66:** a) Raman measurement points for apatite inside the HT-D-PEC. (not to scale) b) Frequency shift of the 960 cm<sup>-1</sup> band against FWHM. c) and d) Raman spectra of in HT-D-PEC irradiated and pristine apatite (in cm<sup>-1</sup>). Raman bands of the pristine apatite are displayed (fitted with Fityk).

For analyzing the spectra, Fityk was used with a pseudovoigt peak shape (Wojdyr (2010)). The linear background and the fitted area was set 100-1400 cm<sup>-1</sup> and 425-525 cm<sup>-1</sup>. Figure 66 shows the overview of the Raman spectra obtained ex situ on different spots of  $\alpha$ -quartz. Generally, all Raman bands of the pristine quartz shifted 5-7 cm<sup>-1</sup> to lower wavenumbers compared to the literature (table 5).

The top of the crystal (Figure 66, nr. 1) shows the highest amorphization in the Raman spectra, as all peaks diminished except for the 128 cm<sup>-1</sup>, 207 cm<sup>-1</sup> and 464 cm<sup>-1</sup> bands. The irradiated quartz spots exhibit higher background intensities (up to 2000 a.u. higher). Further, the 464 cm<sup>-1</sup> decreased its intensity by 90% (pristine: 11388 a.u., irradiated nr.1: 1120 a.u.).

Raman bands of quartz $[cm^{-1}]$		symmetry	source
HT-D-PEC	after literature		
122	128	E <sub>t+1</sub>	Meawad et al. (2025)
201	207	$A_1$	Asell & Nicol (1968)
258	265	$E_{t+1}$	Meawad et al. (2025)
349	356	$A_1$	Asell & Nicol (1968)
397	394	Et	Meawad et al. (2025)
459	464	$A_1$	Asell & Nicol (1968)
502	509	$E_1$	Asell & Nicol (1968)
690	696	$E_{t+1}$	Meawad et al. (2025)
801	807	$E_1$	Meawad et al. (2025)

**Table 5:** Frequencies and modes of Raman bands observed in the non-irradiated  $\alpha$ -quartz

After irradiation, the Raman bands of quartz shifted to lower wavenumbers. The pristine quartz was at 458.66 cm<sup>-1</sup>, the spots nr. 2-5 at 458.26 cm<sup>-1</sup>, and nr.1 at 457.10 cm<sup>-1</sup>. The pristine quartz showed an FWHM 10.21 cm<sup>-1</sup> for the 454 cm<sup>-1</sup> band (Figure 66b). Except for spot nr. 4 with 9.32 cm<sup>-1</sup>, the FWHM shifted to higher values (10.49 cm<sup>-1</sup>).



**Figure 67:** a) Raman measurement points for apatite inside the HT-D-PEC. (not to scale) b) Frequency shift of the 960 cm<sup>-1</sup> band against FWHM. c) and d) Raman spectra of in HT-D-PEC irradiated and pristine apatite (in cm<sup>-1</sup>). Raman bands of the pristine apatite are displayed (fitted with Fityk).

Figure 67 shows an overview of the pristine apatite and the apatite irradiated inside the HT-D-PEC. For apatite, the linear background and the fitted areas were set to 400-1400 cm<sup>-1</sup> and 925-975 cm<sup>-1</sup>.

After irradiation, the Raman bands of apatite shifted to lower wavenumbers. The pristine apatite was at 960.48 cm<sup>-1</sup> and shifted about 6.82 cm<sup>-1</sup> for the irradiated apatite (to 953.66 cm<sup>-1</sup> at spot nr. 5). The background of the irradiated apatite decreased. Further the 447 cm<sup>-1</sup>, 431 cm<sup>-1</sup>, 591 cm<sup>-1</sup> and 608 cm<sup>-1</sup> peaks diminished. The FWHM of the irradiated apatite varied between 7.41-7.63 cm<sup>-1</sup>, whereas the pristine apatite exhibits a FWHM of 7.50 cm<sup>-1</sup> (Figure 67b).

Raman bands of apatite $[cm^{-1}]$		symmetry	source		
	HT-D-PEC	heated	after literature		
	431	423	430	$v_{2b}(E_{1g}); v_2[PO_4^{3-}]$	J. Liu et al. (2008); P. Yuan et al. (2022)
	447		453	$v_{2b}(A_g)$	J. Liu et al. (2008)
	582	584	587	$v_4[PO_4^{3-}]$	P. Yuan et al. (2022)
	591		591	$v_{4b}(E_{1g}+A_g)$	J. Liu et al. (2008)
	608	600	608	$v_{4a}(A_g); v_4[PO_4^{3-}]$	J. Liu et al. (2008); P. Yuan et al. (2022)
	960	954	964	$v_1(A_g); v_1[PO_4^{3-}]$	J. Liu et al. (2008); P. Yuan et al. (2022)
	1040	1036	1042	$v_{3c}(E_{1g})$	Comodi et al. (2001)

Table 6: Frequencies and modes of Raman bands observed in the non-irradiated apatite.

The heated apatite without pressure shows higher intensities than the irradiated apatite. The heated pristine apatite shows wavenumbers  $9-2 \text{ cm}^{-1}$  lower (except for the 587 cm<sup>-1</sup> band) compared to the pristine apatite under pressure (table 6). The 591 cm<sup>-1</sup> band was not observed in the heated apatite (Figure 68). The Raman bands of 423 cm<sup>-1</sup>, 481 cm<sup>-1</sup>, 581 cm<sup>-1</sup> and 600 cm<sup>-1</sup> diminished for the irradiated and heated apatite. The 953.69 cm<sup>-1</sup> line for the pristine apatite shifts only 0.44 cm<sup>-1</sup> to lower wavenumbers (Figure 68d).



**Figure 68:** a) Raman measurement points for heated and irradiated apatite. (not to scale) b) Frequency shift of the 960 cm<sup>-1</sup> band against FWHM. c) and d) Raman spectra of irradiated and pristine apatite (in cm<sup>-1</sup>). Raman bands of the pristine apatite are displayed (fitted with Fityk).

The FWHM of the irradiated apatite varied between 7.61-8.01 cm<sup>-1</sup>, whereas the pristine apatite exhibits a FWHM of 7.73 cm<sup>-1</sup> (Figure 68b). The variance of FWHM in the only heated and irradiated apatite is doubled compared to that of the apatite heated, under pressure and irradiated.

# VIII. Discussion and conclusion

Especially in Earth and Materials science, it is desirable to cover a wide temperature range with HP experimental instruments. Such in-situ conditions for macroscopic samples can be provided by the modified Paris-Edinburgh cell with diamond windows. Here, this Paris-Edinburgh press, equipped with two diamond windows and open single-toroidal anvils, was employed for the first time. The present thesis investigates the application of the D-PEC, utilizing spectroscopic and optical methods similar to those employed for the DAC. This approach aims to demonstrate the diverse capabilities of the D-PEC. Following the technical challenges and failures during the development of the open anvils, diamond window and the HT setup are discussed. So far, the combination of in-situ measurements at ambient and high temperatures has not been published for macroscopic samples in the Paris-Edinburgh cell. Moreover, discussion is made to the calibration series and prospective future refinements.

# VIII.1. Failure investigation of one-sided spherical diamond

Anvil failure occurred during experimental sessions. An one-sided spherical diamond window implemented in the lower anvil disintegrated into dust. When a liquid sample was in direct contact with anvils of any superhard material (tungsten carbide, sintered diamond, cBN, etc.), anvil failure can occur at 3-4 GPa. Similar anvil failures are often observed when samples undergo phase transitions under pressure (Klotz (2012)). In general, the lifetime of anvils can be significantly extended by using encapsulated gaskets, which is not feasible in our case of the D-PEC. The substitution of the one-sided spherical diamond with the conical diamond prevented the slippage of the diamond, thereby extending the lifespan of the anvils.



Figure 69: Photos of broken single-toroidal anvils.
### VIII.2. D-PEC at ambient temperature

The D-PEC was applied for the first time with an optical imaging and spectroscopic setup (see Chapter IV). In the experiment, the phase transition of water to (probably) ice VI was optically observed. Figure 70 illustrates the sample pressure obtained by the peak shift of ruby and the point of the water to ice transition.



Figure 70: Diagram of the calculated sample pressure against oil pressure for the RT gasket (at 298 K).

However, the Raman measurements of ice did not exhibit the characteristic Raman bands of ice VI (Figure 19). Subsequent experiments involving the water-to-ice transition, incorporating an additional pressure gauge such as ruby, are imperative to substantiate the findings of this study.

### VIII.3. Development of the HT-D-PEC

The first prototype of the HT-D-PEC proved to be not feasible (see Chapter V). The developed cooling sleeves limited the space for gasket mounting and placing the gasket assembly in the Paris-Edinburgh cell was laborious. Therefore, internal cooling anvils, stacked behind the open single-toroidal anvils were developed, providing a more efficient cooling performance.

Further, the CuBe-NaCl gasket assembly was redesigned, as the salt showed thinned recrystallization between the anvils, favoring anvil contact. NaCl, while a good choice for its pressure uniformity and transparency to X-rays, might not be the best for high-temperature applications due to its tendency to deform plastically. Therefore, the CuBe-pyrophyllite-NaCl gasket was developed, where the pyrophyllite impeded the extrusion of the salt. An Inconel oven replaced the brittle graphite oven. This CuBe-pyrophyllite-NaCl gasket with an Inconel oven proved to be stable in its power output to temperature ratio and in its pressure resistance up to 5 GPa and 1000 K (Figure 46).

Next step would be a calibration series up to 10 GPa, to be conducted in the full pressure range of the HT-D-PEC. Further, a calibration with inserted thermocouple and pressure gauge should be also conducted. Therefore the split NaCl gasket should be implemented. This kind of calibration could address the pressure component during heating.

Another source of error is the thermal gradient, which has to be investigated. The Section VI.3.1 discusses temperature calibration with K-type thermocouples, but the potential impact of thermal gradients within the sample chamber is less explored. These gradients can affect the accuracy of pressure measurements and the uniformity of sample conditions. Implementing additional temperature measurement points or employing computational thermal simulations to map temperature distribution might provide better control and understanding of the experimental conditions. Additional thermocouple experiments to verify the results in Chapter VI should be attempted.

Furthermore, the pressure gradient inside the sample chamber should be verified. This could be done by implementing several ruby and samarium-doped strontium borate samples in different depths of the sample chamber.

### VIII.4. Irradiation experiments

The PEC with innovative gasket assembly with diamond windows offers a defined spectroscopic and optical channel and an ion radiation pathway as well as relatively high pressure limits. Since the developed D-PEC transmits a wide frequency range of electromagnetic radiation, it can be used at all types of accelerator facilities, including heavy ion accelerators. With the modified HT-D-PEC also the radioactive decay in the Earth's interior could be simulated by combining HP research with ion irradiation.

In the given beam time only one experiment with the HT-D-PEC was possible. The experiment was a feasibility test of the gasket assembly and showed that the oven kept function during the beam time.

For the irradiated quartz, all spectra showed a shift of  $5-7 \text{ cm}^{-1}$  for the Raman bands of quartz compared to the literature (Asell & Nicol (1968); Meawad et al. (2025)). Probably this was caused by a misalignment of the spectrometer. Generally, the irradiated quartz shows an amorphization, visible in the disappearance of several peaks and the decreasing of

the Raman signal intensities (Figure 66).

Due to the application of a heater, two samples of apatite could be irradiated. To determine the influence of the pressure component, the irradiated apatite at elevated temperature were compared with the irradiated apatite at elevated pressure and temperature.

The peak at 954–964 cm<sup>-1</sup> is the strongest characteristic peak of apatite and represents a symmetrical stretching vibration of  $v_1$  [PO<sub>4</sub><sup>3-</sup>] (Comodi et al. (2001)). The Ca-O and Ca-F bonds below 400 cm<sup>-1</sup> can hardly be observed (Schouwink et al. (2010)). A weak absorption peak at 428 cm<sup>-1</sup> ( $v_2$ ) is caused by the bending vibration of [PO<sub>4</sub><sup>3-</sup>] (P. Yuan et al. (2022)). The peak at 588 cm<sup>-1</sup> is the anti-symmetric bending vibration of  $v_4$  [PO<sub>4</sub><sup>3-</sup>] (B. Xu et al. (2020)). In apatite, the phosphate mode of  $v_{3c}$  ( $E_{1g}$ ) and  $v_{4b}$  ( $E_{1g}$ +A<sub>g</sub>) are only observed, when the laser is perpendicular to the c-axis (Comodi et al. (2001)). The 608 cm<sup>-1</sup> is attributed to the  $v_4$  [PO<sub>4</sub><sup>3-</sup>], an antisymmetric bending mode (Schouwink et al. (2010); P. Yuan et al. (2022)). The 1147 cm<sup>-1</sup> band could be attributed to the vibration of [SO<sub>4</sub><sup>2-</sup>] at 1123 cm<sup>-1</sup> (B. Xu et al. (2020)).

At the heavy-ion accelerator (GSI), the HT-D-PEC was prepared and tested for experiments, which can also be performed by external researchers in the future. The combination of accelerated heavy ions and variable pressures and temperatures expands the research on condensed matter for macroscopic sample volumes. Insights from nondestructive quantification of crystal defects at variable pressure and temperature will improve thermochronology dating methods. Crystal defects affect the annealing behavior of natural ion tracks and the diffusion behavior of noble gases. This also applies to the in-situ visualization of processes in the sample chamber and Raman spectroscopy. In-situ spectroscopic analysis (Raman, fluorescence) on macroscopic natural minerals in Cave A is innovative and expands the future analysis possibilities. The D-PEC and HT-D-PEC with innovative gasket assemblies are unique in their design and were built, adapted and tested for studying condensed matter with accelerated ions. The D-PEC would be available for researchers as a permanently installed method in Cave A or in the future in the APPA-Cave at FAIR. In future, there will be a fast-exchangeable toroidal diamond anvils chambers provided by A. Blum, which allows the irradiation of several samples in the same beam time. So that the experimental station "irradiation of matter under extreme conditions" at GSI can be used effectively and by many scientists, the final technical work goal must be the design, construction and testing of a "sample chamber preparation station" with "simple, interchangeable gaskets" for the D-PEC. Irradiation series can be carried out in this way.

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# IX. Appendix



Figure 71: Different load frames of the Paris-Edinburgh press

### Preparation of steel-silver gasket

Preparation of steel-silver gasket Materials

- Silver rod (Ø 6 mm)
- Steel gasket (Ø 15.0-15.5 mm)
- One-sided spherical diamond
- Stainless steel thin plate foil (Ø 9 mm)

#### Devices

- Prepressing jig
- Gasket mounting jig
- Tapered piston attachment
- Workshop press
- Lathe
- Silver-drilling jigs
- Bunsen burner
- Optional: rotary tool with attached aluminum oxide grinding stone or sandpaper (grit size 600)
- 1. Cut silver with pipe cutter
- 2. Prepressing with prepressing jig
  - a Cut 9 mm in length (2.9-3.3 g)
  - b Anneal silver with Bunsen burner -> silver should glow dark red (cherry red)
- 3. Assembling with gasket mounting jig
  - a Put prepressing jig on solid plate of workshop press
  - b Insert first plunger
  - c Insert silver rod with pointed side downwards (towards first plunger)
  - d Insert second plunger
  - e Insert a steel thin plate foil
  - f Slowly built up pressure to 90 bar (1 min)

- g Rest 1 min
- h Release pressure slowly
- 4. Drilling sample chamber at lathe (in 3 jaw chucks)
  - a Put mounting jig on solid plate of workshop press
  - b Insert bottom plunger with diamond indentation
     Note: hole (of the plunger) below diamond indentation should be filled with modelling clay/wax
  - c Insert prepressed silver and steel gasket
  - d Insert upper plunger (without diamond indentation)
  - e Insert a steel thin plate foil
  - f Slowly built up pressure to 90 bar (1 min)
  - g Rest 1 min
  - h Release pressure slowly



Figure 72: Drilling sample chamber at lathe (in 3 jaw chucks)

- 5. Finishing sample chamber
  - a Insert steel-silver gasket assembly in silver-drilling jig
  - b Drill hole with mm (carbide bit) Set lathe with speed: 640 U/min. Add cutting oil
  - c Change direction of gasket and drill from other side
  - d Drill with .5 mm (carbide bit)
  - e Clamp silver-drilling jig in vise

- f Remove splinters with rotary tool (polish attachment) or by hand with grinding paper
- g Clean sample chamber with water and vent
- 6. Merging diamond with mounting jig
  - a Put mounting jig on solid plate of workshop press
  - b Insert bottom plunger with diamond indentation
  - c Insert diamond and prepressed steel-silver gasket Note: table face of diamond should be horizontal!!!
  - d Insert upper two-part plunger
  - e Insert a steel thin plate foil
  - f Built pressure up to <110 bar
  - g Rest 2 min
  - h Release pressure slowly

Table 7: Magnification and working distance of the long-distance microscope with different objectives

objective	working distance [mm]	primary	10x ocular
CF-1	300	13,2 x	132 x
	500	7,5 x	75 x
	700	5,3 x	53 x
CF-2	150	24 x	240 x
	180	19 x	190 x
	220	15 x	150 x
CF-3	100	33 x	330 x
	115	28 x	280 x
	130	24 x	240 x
CF-4	48	63 x	630 x
	53	55 x	550 x
	58	49 x	490 x

## Aligning of LDM to D-PEC

Initial

- Loaded D-PEC in horizontal position
- Check LDM for loose tubes/parts
- Mount LDM on 2 clamps (but put aside from beam line)

Caution: Dont look in the direction of laser! Wear safety goggles.



Figure 73: Aligning of LDM to D-PEC

- 1. Align Raman probe to D-PEC, without LDM (remove LDM incl. rings)
  - Using paper with pin hole ( $\emptyset$ :  $\sim$ 1 mm = around laser diameter)
  - Glue with double-sided sticky tape (by Tesa) Si-Wafer as mirror on D-PEC channel
    - Move PEC and LDM, tilt to align mirrored laser on pinhole
    - Note orientation angel on table
- 2. Align beam to D-PEC center
  - a Use reflection in channel for top-bottom (beam out of horizontal center)
  - b Then do left-right adjustments
    - Do NOT rotate; only x + z changes
    - Optimize for laser intensity at back of D-PEC
- 3. Add LDM to beam line
  - Align posts (holders of LDM) along laser

- Optically center rear end to Raman probe
- a Rear end centering is prepared by bringing laser beam to center of front lens
  - Gradually close aperture and optimize centering of intensity
- b Then optimize front end (might require re-adjusting rear!)
  - By: small (but intense) reflection of laser at mirror visible on front lens
  - Keep aperture quite closed  $\sim$ 30% -> reopen for readjusting rear (if needed)
- 4. Align with aligned LDM, align whole set up in y+z again by
  - D-PEC rear intensity (maybe use channel wall again)
- 5. Open aperture to 80% or 100% (Raman mode (switch box))
  - a Find focal plane (in video mode; in transmitted light, laser: 10 mW)
    - Move y (= focus) to find inversion point of astigmatism; beam defocusing
  - b Optimize transmitted light (in video mode) / if possible
    - Position + focus
  - c Optimize intensity of counts (fluorescence of Rb/Sr/Dia etc.; laser: 10-30 mW)
    - Try y (=focus), when reaching visible counts (in RTD mode), alternate y+z+x
  - d Optimize aperture:
    - Close from 100% open aperture till 80-90% of counts are still visible (aperture is probably 40-60% closed)



Figure 74: Boron-doped diamond



**Figure 75:** a) Fitted ruby peaks at 0 bar oil pressure. b) Fitted ruby peaks at 100 bar oil pressure. c) Fitted ruby peaks at 700 bar oil pressure. d) Fitted quartz peak at 0 bar oil pressure. e) Fitted quartz peak at 100 bar oil pressure. f) Fitted quartz peak at 700 bar oil pressure.

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Table

oil P	error	direction	peak pos.	abs. error	rel. error	amplitude	abs. error	rel. error	FWHM	abs. error	rel. error	peak shift	Rb P calc	error
[bar]	[bar]		[um]	[uu]	[%]	[a.u.]	[a.u.]	[%]	[uu]	[nm]	[%]	[uu]	[GPa]	[GPa]
0	2.00	down	464.34	9.634E-02	0.02	14386.85	813.26	5.65	9.93	0.3823312	3.85	0.00	0.00	0.05
94	2.09	down	483.50	3.279E-02	0.01	24314.37	401.48	1.65	9.61	0.11816532	1.23	19.16	2.26	0.05
191	2.19	down	490.17	2.565E-02	0.01	31614.81	443.04	1.40	8.71	0.09793062	1.12	25.83	3.10	0.05
285	2.29	down	494.60	2.481E-02	0.01	36762.14	571.27	1.55	8.94	0.09380838	1.05	30.26	3.69	0.05
377	2.38	down	496.85	2.836E-02	0.01	41437.86	785.68	1.90	8.98	0.1107866	1.23	32.51	3.99	0.05
463	2.46	down	498.30	2.521E-02	0.01	46892.55	862.86	1.84	9.32	0.09641594	1.03	33.96	4.18	0.05
529	2.53	down	499.44	3.064E-02	0.01	36689.58	857.87	2.34	9.17	0.11933754	1.30	35.10	4.34	0.05
568	2.57	down	498.69	2.000E-02	0.00	68957.52	1049.30	1.52	9.22	0.07429146	0.81	34.35	4.23	0.05
597	2.60	down	499.05	2.017E-02	0.00	68593.47	1017.97	1.48	9.02	0.08023432	0.89	34.71	4.28	0.05
20	2.02	dn	464.42	9.639E-02	0.02	43970.37	2443.98	5.56	11.33	0.39313656	3.47	0.08	0.01	0.05
30	2.03	dn	464.94	7.846E-02	0.02	72650.64	3213.67	4.42	9.92	0.318517	3.21	0.60	0.07	0.05
40	2.04	dn	466.58	5.772E-02	0.01	58891.83	1804.29	3.06	10.05	0.23368912	2.33	2.24	0.25	0.05
55	2.06	dn	468.24	4.999E-02	0.01	39425.76	1052.52	2.67	10.05	0.1887622	1.88	3.90	0.44	0.05
70	2.07	dn	470.12	4.693E-02	0.01	35348.11	816.12	2.31	9.20	0.18964272	2.06	5.78	0.65	0.05
85	2.09	dn	471.55	5.847E-02	0.01	25165.44	729.38	2.90	9.62	0.22353444	2.32	7.21	0.82	0.05
100	2.10	dn	472.72	4.129E-02	0.01	23352.28	455.32	1.95	9.57	0.16340232	1.71	8.38	0.95	0.05
115	2.12	dn	473.44	4.434E-02	0.01	23711.31	515.33	2.17	9.57	0.16679722	1.74	9.10	1.04	0.05
130	2.13	dn	473.85	4.443E-02	0.01	24838.37	528.69	2.13	9.37	0.1715743	1.83	9.51	1.09	0.05
145	2.15	dn	474.41	3.634E-02	0.01	28884.66	493.89	1.71	9.34	0.1422651	1.52	10.07	1.15	0.05
160	2.16	dn	474.67	5.711E-02	0.01	15142.07	416.49	2.75	9.10	0.2197509	2.41	10.33	1.18	0.05
175	2.18	dn	476.84	5.922E-02	0.01	14895.96	417.60	2.80	9.20	0.22731956	2.47	12.50	1.44	0.05
190	2.19	dn	477.08	5.480E-02	0.01	13288.27	339.33	2.55	9.19	0.21374786	2.33	12.74	1.47	0.05
205	2.21	dn	478.29	4.548E-02	0.01	16065.49	355.31	2.21	9.09	0.16994954	1.87	13.95	1.62	0.05
220	2.22	dn	479.14	4.097E-02	0.01	18574.12	347.96	1.87	8.87	0.1648156	1.86	14.80	1.72	0.05
235	2.24	dn	479.97	4.272E-02	0.01	18708.15	379.43	2.03	9.03	0.16374044	1.81	15.63	1.82	0.05
250	2.25	dn	480.89	4.760E-02	0.01	20526.85	460.74	2.24	9.17	0.1830633	2.00	16.55	1.93	0.05
265	2.27	dn	481.55	4.342E-02	0.01	17972.52	357.26	1.99	8.98	0.17455838	1.94	17.21	2.01	0.05
272	2.27	dn	480.88	5.100E-02	0.01	15345.66	369.38	2.41	9.17	0.19595246	2.14	16.54	1.93	0.05
280	2.28	dn	482.37	3.969E-02	0.01	19836.12	380.88	1.92	9.32	0.14888702	1.60	18.03	2.12	0.05
295	2.30	dn	481.07	7.692E-02	0.02	11155.73	393.39	3.53	9.41	0.30180164	3.21	16.73	1.96	0.05
310	2.31	dn	482.50	9.306E-02	0.02	8552.15	369.47	4.32	9.48	0.36198022	3.82	18.16	2.13	0.05

	1	-		-	-	-	-	-		-		-		-		-		-		1	,
error	[GPa]	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Rb P_calc	[GPa]	2.35	2.40	2.51	2.62	2.71	2.81	2.86	2.98	3.11	3.21	3.31	3.45	3.53	3.72	3.81	3.90	4.00	4.10	4.30	4.41
peak shift	[uu]	19.93	20.29	21.16	22.08	22.75	23.58	23.96	24.90	25.89	26.66	27.40	28.45	29.11	30.50	31.22	31.85	32.64	33.35	34.86	35.68
rel. error	[%]	4.27	4.01	2.55	3.70	2.74	2.62	2.05	1.58	1.55	1.49	1.48	1.23	1.17	1.22	1.28	1.35	1.20	1.25	1.49	0.95
abs. error	[nm]	0.42509448	0.38705432	0.24769962	0.34503788	0.24246868	0.23401098	0.18247852	0.1416431	0.13517544	0.12834954	0.13497692	0.11217868	0.10552474	0.11340644	0.11846022	0.12675362	0.11032792	0.11695124	0.13650832	0.09233276
FWHM	[uu]	9.97	9.65	9.72	9.33	8.84	8.92	8.91	8.98	8.70	8.62	9.15	9.13	9.03	9.26	9.27	9.37	9.17	9.34	9.15	9.67
rel. error	[%]	4.96	5.12	3.44	4.63	3.20	3.15	2.51	2.07	1.96	1.81	2.14	1.81	1.84	2.00	2.09	2.42	1.95	2.23	2.57	1.97
abs. error	[a.u.]	405.67	407.47	376.48	536.26	410.20	470.28	469.19	432.02	452.77	457.47	578.23	529.28	544.58	649.92	699.84	829.85	726.58	796.80	937.53	938.13
amplitude	[a.u.]	8184.37	7951.86	10933.47	11575.26	12803.01	14948.77	18703.79	20869.63	23107.36	25261.9	27081.77	29235.01	29597.89	32449.71	33424.31	34249.32	37202.63	35753.63	36456.78	47723.08
rel. error	[%]	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
abs. error	[uu]	1.080E-01	1.041E-01	6.796E-02	9.185E-02	6.308E-02	6.106E-02	4.797E-02	3.808E-02	3.561E-02	3.297E-02	3.668E-02	3.030E-02	2.927E-02	3.094E-02	3.186E-02	3.502E-02	2.870E-02	3.109E-02	3.451E-02	2.431E-02
peak pos.	[um]	484.27	484.63	485.50	486.42	487.09	487.92	488.30	489.24	490.23	491.00	491.74	492.79	493.45	494.84	495.56	496.19	496.98	497.69	499.20	500.02
direction		dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn						
error	[bar]	2.33	2.34	2.36	2.37	2.39	2.40	2.42	2.43	2.45	2.46	2.48	2.49	2.51	2.53	2.55	2.56	2.58	2.59	2.62	2.70
oil P	[bar]	325	340	355	370	385	400	415	430	445	460	475	490	505	530	545	560	575	590	620	700

Table 9: Fitting results of ruby (part 2)

4 :		•	-	-	-	-	-	-		-	-	J. F. F	- -	
011 P	error	direction	peak pos.	abs. error	rel. error	amplitude	abs. error	rel. error	FWHM	abs. error	rel. error	peak shift	RD P_calc	error
[bar]	[bar]		[nm]	[nm]	[%]	[a.u.]	[a.u.]	[%]	[nm]	[nm]	[%]	[nm]	[GPa]	[GPa]
0	2.00	down	464.34	9.634E-02	0.02	14386.85	813.26	5.65	9.93	0.3823312	3.85	0.00	0.00	0.05
94	2.09	down	483.50	3.279E-02	0.01	24314.37	401.48	1.65	9.61	0.11816532	1.23	19.16	2.26	0.05
191	2.19	down	490.17	2.565E-02	0.01	31614.81	443.04	1.40	8.71	0.09793062	1.12	25.83	3.10	0.05
285	2.29	down	494.60	2.481E-02	0.01	36762.14	571.27	1.55	8.94	0.09380838	1.05	30.26	3.69	0.05
377	2.38	down	496.85	2.836E-02	0.01	41437.86	785.68	1.90	8.98	0.1107866	1.23	32.51	3.99	0.05
463	2.46	down	498.30	2.521E-02	0.01	46892.55	862.86	1.84	9.32	0.09641594	1.03	33.96	4.18	0.05
529	2.53	down	499.44	3.064E-02	0.01	36689.58	857.87	2.34	9.17	0.11933754	1.30	35.10	4.34	0.05
568	2.57	down	498.69	2.000E-02	0.00	68957.52	1049.30	1.52	9.22	0.07429146	0.81	34.35	4.23	0.05
597	2.60	down	499.05	2.017E-02	0.00	68593.47	1017.97	1.48	9.02	0.08023432	0.89	34.71	4.28	0.05
20	2.02	dn	464.42	9.639E-02	0.02	43970.37	2443.98	5.56	11.33	0.39313656	3.47	0.08	0.01	0.05
30	2.03	dn	464.94	7.846E-02	0.02	72650.64	3213.67	4.42	9.92	0.318517	3.21	0.60	0.07	0.05
40	2.04	dn	466.58	5.772E-02	0.01	58891.83	1804.29	3.06	10.05	0.23368912	2.33	2.24	0.25	0.05
55	2.06	dn	468.24	4.999E-02	0.01	39425.76	1052.52	2.67	10.05	0.1887622	1.88	3.90	0.44	0.05
70	2.07	dn	470.12	4.693E-02	0.01	35348.11	816.12	2.31	9.20	0.18964272	2.06	5.78	0.65	0.05
85	2.09	dn	471.55	5.847E-02	0.01	25165.44	729.38	2.90	9.62	0.22353444	2.32	7.21	0.82	0.05
100	2.10	dn	472.72	4.129E-02	0.01	23352.28	455.32	1.95	9.57	0.16340232	1.71	8.38	0.95	0.05
115	2.12	dn	473.44	4.434E-02	0.01	23711.31	515.33	2.17	9.57	0.16679722	1.74	9.10	1.04	0.05
130	2.13	dn	473.85	4.443E-02	0.01	24838.37	528.69	2.13	9.37	0.1715743	1.83	9.51	1.09	0.05
145	2.15	dn	474.41	3.634E-02	0.01	28884.66	493.89	1.71	9.34	0.1422651	1.52	10.07	1.15	0.05
160	2.16	dn	474.67	5.711E-02	0.01	15142.07	416.49	2.75	9.10	0.2197509	2.41	10.33	1.18	0.05
175	2.18	dn	476.84	5.922E-02	0.01	14895.96	417.60	2.80	9.20	0.22731956	2.47	12.50	1.44	0.05
190	2.19	dn	477.08	5.480E-02	0.01	13288.27	339.33	2.55	9.19	0.21374786	2.33	12.74	1.47	0.05
205	2.21	dn	478.29	4.548E-02	0.01	16065.49	355.31	2.21	9.09	0.16994954	1.87	13.95	1.62	0.05
220	2.22	dn	479.14	4.097E-02	0.01	18574.12	347.96	1.87	8.87	0.1648156	1.86	14.80	1.72	0.05
235	2.24	dn	479.97	4.272E-02	0.01	18708.15	379.43	2.03	9.03	0.16374044	1.81	15.63	1.82	0.05
250	2.25	dn	480.89	4.760E-02	0.01	20526.85	460.74	2.24	9.17	0.1830633	2.00	16.55	1.93	0.05
265	2.27	dn	481.55	4.342E-02	0.01	17972.52	357.26	1.99	8.98	0.17455838	1.94	17.21	2.01	0.05
272	2.27	dn	480.88	5.100E-02	0.01	15345.66	369.38	2.41	9.17	0.19595246	2.14	16.54	1.93	0.05
280	2.28	dn	482.37	3.969E-02	0.01	19836.12	380.88	1.92	9.32	0.14888702	1.60	18.03	2.12	0.05
295	2.30	dn	481.07	7.692E-02	0.02	11155.73	393.39	3.53	9.41	0.30180164	3.21	16.73	1.96	0.05
310	2.31	dn	482.50	9.306E-02	0.02	8552.15	369.47	4.32	9.48	0.36198022	3.82	18.16	2.13	0.05

Table 10: Fitting results of quartz (part 1)

										·				-		-		-		-	<b></b>
error	[GPa]	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Rb P_calc	[GPa]	2.35	2.40	2.51	2.62	2.71	2.81	2.86	2.98	3.11	3.21	3.31	3.45	3.53	3.72	3.81	3.90	4.00	4.10	4.30	4.41
peak shift	[um]	19.93	20.29	21.16	22.08	22.75	23.58	23.96	24.90	25.89	26.66	27.40	28.45	29.11	30.50	31.22	31.85	32.64	33.35	34.86	35.68
rel. error	[%]	4.27	4.01	2.55	3.70	2.74	2.62	2.05	1.58	1.55	1.49	1.48	1.23	1.17	1.22	1.28	1.35	1.20	1.25	1.49	0.95
abs. error	[uu]	0.42509448	0.38705432	0.24769962	0.34503788	0.24246868	0.23401098	0.18247852	0.1416431	0.13517544	0.12834954	0.13497692	0.11217868	0.10552474	0.11340644	0.11846022	0.12675362	0.11032792	0.11695124	0.13650832	0.09233276
FWHM	[uu]	9.97	9.65	9.72	9.33	8.84	8.92	8.91	8.98	8.70	8.62	9.15	9.13	9.03	9.26	9.27	9.37	9.17	9.34	9.15	9.67
rel. error	[%]	4.96	5.12	3.44	4.63	3.20	3.15	2.51	2.07	1.96	1.81	2.14	1.81	1.84	2.00	2.09	2.42	1.95	2.23	2.57	1.97
abs. error	[a.u.]	405.67	407.47	376.48	536.26	410.20	470.28	469.19	432.02	452.77	457.47	578.23	529.28	544.58	649.92	699.84	829.85	726.58	796.80	937.53	938.13
amplitude	[a.u.]	8184.37	7951.86	10933.47	11575.26	12803.01	14948.77	18703.79	20869.63	23107.36	25261.9	27081.77	29235.01	29597.89	32449.71	33424.31	34249.32	37202.63	35753.63	36456.78	47723.08
rel. error	[%]	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
abs. error	[uu]	1.080E-01	1.041E-01	6.796E-02	9.185E-02	6.308E-02	6.106E-02	4.797E-02	3.808E-02	3.561E-02	3.297E-02	3.668E-02	3.030E-02	2.927E-02	3.094E-02	3.186E-02	3.502E-02	2.870E-02	3.109E-02	3.451E-02	2.431E-02
peak pos.	[uu]	484.27	484.63	485.50	486.42	487.09	487.92	488.30	489.24	490.23	491.00	491.74	492.79	493.45	494.84	495.56	496.19	496.98	497.69	499.20	500.02
direction		dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn						
error	[bar]	2.33	2.34	2.36	2.37	2.39	2.40	2.42	2.43	2.45	2.46	2.48	2.49	2.51	2.53	2.55	2.56	2.58	2.59	2.62	2.70
oil P	[bar]	325	340	355	370	385	400	415	430	445	460	475	490	505	530	545	560	575	590	620	700

Table 11: Fitting results of quartz (part 2)



Figure 76: Gasket assembly tool



**Figure 77:** Cooling anvils and plastic sleeves of the HT-D-PEC. (1) Cooling anvils, (2) upper plastic sleeve and (3) lower plastic sleeve

experiment	filename	start	end	mask	
002_PEB	RbSr_0014_bar_u_000_cV_02	692.5	697.0	695.0	696.5
002_PEB	RbSr_0060_bar_u_075_cV_01	692.0	698.0	695.4	696.5
002_PEB	RbSr_0060_bar_u_100_cV_0min	692.5	697.0	695.5	696.5
002_PEB	RbSr_0060_bar_u_100_cV_1min	692.5	697.0	695.5	696.5
002_PEB	RbSr_0060_bar_u_100_cV_4min	692.5	697.0	695.5	696.5
002_PEB	RbSr_0060_bar_u_100_cV_7min	692.5	697.0	695.5	696.5
002_PEB	RbSr_0075_bar_u_100_cV_01	692.5	698.0	695.5	696.0
002_PEB	RbSr_0089_bar_u_100_cV_01	692.5	698.0	695.3	696.3
002_PEB	RbSr_0135_bar_u_100_cV_01	693.0	697.5		
002_PEB	RbSr_0270_bar_u_000_cV_01	692.5	697.0	695.5	696.7
002_PEB	RbSr_0333_bar_u_000_cV_01	692.5	698.0	695.8	697.0
002_PEB	RbSr_0409_bar_u_000_cV_02	692.5	698.0	696.0	697.0
004_PEB	RbSr_0000_bar_d_000_cV_01	692.0	698.0	695.0	696.0
004_PEB	RbSr_0020_bar_u_000_cV_02	692.0	698.0	695.0	696.0
004_PEB	RbSr_0060_bar_u_050_cV_01	692.0	698.0	695.0	696.0
004_PEB	RbSr_0060_bar_u_070_cV_01	692.0	698.0	695.4	696.0
004_PEB	RbSr_0060_bar_u_090_cV_01	692.0	698.0		
004_PEB	RbSr_0090_bar_u_100_cV_01	692.0	698.0		
004_PEB	RbSr_0130_bar_u_000_cV_02	692.5	698.0	695.0	696.5
004_PEB	RbSr_0200_bar_u_000_cV_02	692.5	698.0	695.3	696.0
004_PEB	RbSr_0270_bar_u_000_cV_01	692.0	698.0	695.3	696.5
004_PEB	RbSr_0328_bar_u_000_cV_02	692.0	698.0	695.3	696.5
004_PEB	RbSr_0400_bar_u_000_cV_03	692.0	698.0		
004_PEB	RbSr_0476_bar_u_000_cV_03	692.5	697.0	695.5	696.5
004_PEB	RbSr_0554_bar_u_000_cV_03	692.0	698.0		
004_PEB	RbSr_0599_bar_u_000_cV_01	692.0	698.0	696.0	696.5

Table 12: Fitting range of ruby spectra



Figure 78: Drawing of the cooling anvil



Figure 79: Drawing of the upper plastic sleeve.



Figure 80: Drawing of the lower plastic sleeve.

experiment	filename	start	end
003_PEB	RbSr_0060_bar_u_000_cV_01	684.0	688.0
003_PEB	RbSr_0060_bar_u_060_cV_01	684.0	687.0
003_PEB	RbSr_0060_bar_u_160_cV_03	683.0	692.0
003_PEB	RbSr_0060_bar_u_170_cV_01	683.0	692.0

 Table 13: Fitting range of samarium-doped strontium borate spectra

Table 14: Fitting range of quartz spectra

experiment	filename	start	end
003_PEB	Qzab_0000_bar_d_000_cV_01	400.0	500.0



**Figure 81:** a) Fitted samarium-doped strontium borate peaks at 0 bar oil pressure. b) Fitted samarium-doped strontium borate peaks at 599 bar oil pressure. c) Fitted ruby peaks at 0 bar oil pressure. d) Fitted ruby peak at 599 bar oil pressure. e) Fitted quartz peak at 5 bar oil pressure. f) Fitted quartz peak at 603 bar oil pressure.

PEB)
(002_
borate
strontium
samarium-doped
results of
Fitting
Table 15:

error	[GPa]	0.0015	0.0016	0.0015	0.0030	0.0031	0.0048	0.0047	0.0066	0.0065	0.0084	0.0082	0.0093	0.0002	0.0002	0.0002	0.0002	0.0002	0.0003	0.0003	0.0003	0.0003	0.0004	0.0003	0.0005	0.0010	0.0014	0.0021	0.0027	0.0050	0.0038	0.0061	0.0062	0.0070
Sb P_calc	[GPa]	2.92	2.96	2.88	4.14	4.18	5.19	5.16	6.13	6.05	6.90	6.82	7.25	0.36	0.76	0.60	0.64	0.80	1.24	1.24	1.24	1.28	1.36	1.24	1.56	2.36	2.80	3.47	3.90	5.31	4.61	5.86	5.93	6.28
peak shift	[uu]	0.73	0.74	0.72	1.04	1.05	1.31	1.30	1.55	1.53	1.75	1.73	1.84	0.09	0.19	0.15	0.16	0.20	0.31	0.31	0.31	0.32	0.34	0.31	0.39	0.59	0.70	0.87	0.98	1.34	1.16	1.48	1.50	1 50
rel. error	[%]	0.30	0.29	0.21	0.26	0.24	0.24	0.24	0.29	0.30	0.41	0.40	0.61	0.67	0.59	0.41	0.51	0.44	0.44	0.47	0.44	0.49	0.48	0.53	0.50	2.11	0.47	0.43	0.37	0.83	0.43	0.34	0.66	0 56
abs. error	[nm]	8.549E-04	8.235E-04	5.913E-04	8.435E-04	7.929E-04	8.787E-04	8.680E-04	1.127E-03	1.161E-03	1.698E-03	1.632E-03	2.496E-03	1.980E-03	1.902E-03	8.379E-04	1.056E-03	9.285E-04	1.485E-03	1.582E-03	1.524E-03	1.673E-03	1.616E-03	1.257E-03	1.268E-03	6.931E-03	1.374E-03	1.363E-03	1.196E-03	2.442E-03	1.456E-03	9.434E-04	2.176E-03	1 077E_03
FWHM	[uu]	0.29	0.29	0.28	0.33	0.32	0.36	0.36	0.39	0.39	0.41	0.4	0.41	0.3	0.32	0.2	0.21	0.21	0.34	0.34	0.34	0.34	0.34	0.24	0.25	0.33	0.29	0.32	0.32	0.3	0.34	0.28	0.33	0.05
rel. error	[%]	0.39	0.37	0.28	0.33	0.33	0.32	0.32	0.44	0.42	0.63	0.60	0.89	1.22	1.02	0.51	0.66	0.53	0.72	0.75	0.73	0.79	0.74	0.64	0.61	2.35	0.60	0.56	0.49	0.77	0.56	0.43	0.70	0 7 0
abs. error	[a.u.]	58.89	58.67	39.30	55.90	39.22	51.80	49.79	50.05	65.72	49.91	48.61	57.86	67.82	17.44	4.09	5.23	30.81	18.68	19.19	18.24	19.43	18.05	5.00	4.28	37.87	12.52	13.88	10.38	6.50	11.40	93.20	5.65	116 00
amplitude	[a.u.]	15169.05	15767.02	14263.71	16820.15	11753.65	16119.02	15516.64	11406.17	15516.36	7905.90	8076.16	6499.23	5553.78	1705.91	795.53	792.55	5785.88	2591.18	2568.81	2488.39	2452.60	2434.20	777.10	706.65	1610.03	2099.14	2501.05	2131.71	844.42	2028.83	21586.50	809.34	77 27 200
rel. error	[%]	4.110E-05	3.941E-05	2.846E-05	3.984E-05	3.824E-05	4.114E-05	4.091E-05	5.469E-05	5.516E-05	8.186E-05	7.820E-05	1.178E-04	1.075E-04	1.011E-04	4.033E-05	5.153E-05	4.423E-05	7.734E-05	8.152E-05	7.943E-05	8.643E-05	8.244E-05	5.957E-05	5.967E-05	3.097E-04	6.498E-05	6.452E-05	5.686E-05	1.008E-04	6.868E-05	4.447E-05	9.332E-05	
abs. error	[uu]	2.820E-04	2.704E-04	1.953E-04	2.735E-04	2.625E-04	2.825E-04	2.809E-04	3.757E-04	3.789E-04	5.625E-04	5.374E-04	8.097E-04	7.372E-04	6.934E-04	2.765E-04	3.533E-04	3.032E-04	5.303E-04	5.590E-04	5.447E-04	5.927E-04	5.654E-04	4.085E-04	4.092E-04	2.125E-03	4.458E-04	4.428E-04	3.903E-04	6.922E-04	4.715E-04	3.054E-04	6.411E-04	6 3E1E 04
peak pos.	[uu]	686.15	686.16	686.14	686.46	686.47	686.73	686.72	686.97	686.95	687.17	687.15	687.26	685.51	685.61	685.57	685.58	685.62	685.73	685.73	685.73	685.74	685.76	685.73	685.81	686.01	686.12	686.29	686.40	686.76	686.58	686.90	686.92	607.01
direction		down	dn	411																														
error	[bar]	2.10	2.10	2.11	2.20	2.20	2.30	2.30	2.40	2.40	2.50	2.50	2.59	2.01	2.04	2.05	2.05	2.05	2.06	2.06	2.06	2.06	2.06	2.08	2.09	2.14	2.20	2.27	2.33	2.41	2.42	2.47	2.48	о <u>г</u> б
oil P	[bar]	95	101	105	200	204	296	301	397	401	499	502	593	14	40	48	48	48	60	60	60	61	61	75	89	135	198	270	333	409	417	466	480	560

error	[GPa]	0.0808	0.0810	0.0810	0.0810	0.0821	0.0812	0.0813	0.0814	0.0818	0.0826	0.0826	0.0827	0.0821	0.0824	0.0829	0.0836	0.0842
Rb P_calc	[GPa]	0.05	0.43	0.46	0.57	1.76	0.76	0.78	1.00	1.43	2.20	2.06	2.11	1.68	1.98	2.44	2.91	3.35
peak shift	[uu]	0.02	0.16	0.17	0.21	0.65	0.28	0.29	0.37	0.53	0.81	0.76	0.78	0.62	0.73	0.90	1.07	1.23
rel. error	[%]	17.09	2.91	1.56	1.52	4.00	2.87	1.92	2.90	1.33	7.91	3.49	2.97	4.29	6.15	3.90	101.96	11.37
abs. error	[uu]	1.504E-01	1.879E-02	1.064E-02	1.065E-02	5.990E-02	1.802E-02	1.432E-02	2.225E-02	1.448E-02	1.133E-01	5.247E-02	4.230E-02	3.308E-02	5.056E-02	3.804E-02	1.046E+00	1.932E-01
FWHM	[uu]	0.88	0.65	0.68	0.70	1.50	0.63	0.75	0.77	1.09	1.43	1.51	1.42	0.77	0.82	0.98	1.03	1.70
rel. error	[%]	43.10	12.91	6.61	7.48	14.26	11.47	8.05	11.91	3.76	22.44	9.87	6.35	10.11	17.35	13.36	305.95	25.67
abs. error	[a.u.]	297.94	101.33	86.18	84.43	573.08	341.52	379.69	419.88	205.53	982.81	269.13	119.88	428.78	158.60	103.92	1884.90	263.64
amplitude	[a.u.]	691.35	784.87	1304.22	1128.63	4017.90	2977.84	4713.90	3526.04	5470.10	4380.58	2725.59	1886.44	4239.43	913.95	778.15	616.07	1027.23
rel. error	[%]	2.343E-03	7.123E-04	3.944E-04	4.389E-04	1.260E-03	7.267E-04	3.330E-04	4.070E-04	4.565E-04	9.653E-04	1.927E-03	2.017E-03	1.175E-03	9.954E-04	1.089E-03	1.635E-02	3.614E-03
abs. error	[uu]	1.627E-02	4.946E-03	2.738E-03	3.048E-03	8.756E-03	5.047E-03	2.313E-03	2.827E-03	3.172E-03	6.709E-03	1.339E-02	1.402E-02	8.167E-03	6.918E-03	7.568E-03	1.137E-01	2.513E-02
peak pos.	[uu]	694.25	694.39	694.40	694.44	694.88	694.51	694.52	694.60	694.76	695.04	694.99	695.01	694.85	694.96	695.13	695.30	695.46
direction		dn																
error	[bar]	2.01	2.04	2.05	2.05	2.05	2.06	2.06	2.06	2.06	2.06	2.08	2.09	2.14	2.20	2.27	2.33	2.41
oil P	[bar]	14	40	48	48	48	60	60	60	60	60	75	89	135	198	270	333	409

Table 16: Fitting results of ruby (002\_PEB)

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error	[GPa]	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
Sb P_calc	[GPa]	0.0000	0.1209	0.0403	0.0000	0.3222	0.4429	0.5635	0.6036	0.6036	0.6036	0.6438	0.6438	0.6438	0.6839	0.7241	0.7241	0.7642	0.9246
peak shift	[um]	0.00	0.03	0.01	0.00	0.08	0.11	0.14	0.15	0.15	0.15	0.16	0.16	0.16	0.17	0.18	0.18	0.19	0.23
rel. error	[%]	0.60	0.59	1.05	1.22	0.96	0.87	0.67	0.56	0.57	0.53	0.52	0.49	0.54	0.66	0.93	1.84	4.96	19.52
abs. error	[uu]	1.182E-03	1.153E-03	1.985E-03	2.425E-03	1.898E-03	1.906E-03	1.457E-03	1.213E-03	1.251E-03	1.184E-03	1.212E-03	1.200E-03	1.438E-03	1.805E-03	2.718E-03	5.751E-03	1.554E-02	7.089E-02
FWHM	[uu]	0.20	0.20	0.19	0.20	0.20	0.22	0.22	0.22	0.22	0.23	0.23	0.24	0.27	0.27	0.29	0.31	0.31	0.36
rel. error	[%]	0.78	0.74	1.27	1.57	1.42	1.20	1.04	0.69	0.69	0.62	0.58	0.52	0.59	0.65	0.89	1.72	3.78	12.02
abs. error	[a.u.]	15.75	39.40	4.83	2.92	68.70	5.53	10.86	6.63	7.05	6.40	5.43	5.25	4.82	3.76	3.45	3.31	7.74	11.25
amplitude	[a.u.]	2028.18	5289.06	380.27	185.81	4843.81	459.81	1044.91	960.52	1025.39	1026.73	943.80	1003.44	824.03	577.15	388.46	192.47	204.99	93.60
rel. error	[%]	5.762E-05	5.585E-05	9.455E-05	1.180E-04	9.164E-05	9.483E-05	6.965E-05	5.789E-05	5.907E-05	5.555E-05	5.502E-05	5.362E-05	6.432E-05	7.774E-05	1.147E-04	2.387E-04	5.673E-04	2.263E-03
abs. error	[uu]	3.950E-04	3.828E-04	6.481E-04	8.090E-04	6.282E-04	6.501E-04	4.775E-04	3.969E-04	4.050E-04	3.809E-04	3.772E-04	3.676E-04	4.410E-04	5.330E-04	7.863E-04	1.636E-03	3.890E-03	1.552E-02
peak pos.	[um]	685.42	685.45	685.43	685.42	685.50	685.53	685.56	685.57	685.57	685.57	685.58	685.58	685.58	685.59	685.60	685.60	685.61	685.65
voltage	[cV]	0	0	0	50	0	50	60	70	80	90	100	110	120	130	140	150	160	170
direction		down	down	dn															
error	[bar]	2.00	2.02	2.02	2.02	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06
oil P	[bar]	0	20	20	20	60	60	60	60	60	60	60	60	60	61	61	62	64	64

**Table 17:** Fitting results of strontium borate (003\_PEB)

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error	[GPa]	0.0808	0.0808	0.0808	0.0810	0.0809	0.0814	0.0817	0.0821	0.0826	0.0836	0.0844	0.0856	0.0860
Rb P_calc	[GPa]	0.0000	0.0808	0.0808	0.3775	0.2696	0.9454	1.3523	1.7329	2.2235	2.9346	3.5111	4.2276	4.4487
peak shift	[uu]	0	0.03	0.03	0.14	0.1	0.35	0.5	0.64	0.82	1.08	1.29	1.55	1.63
rel. error	[%]	0.43	4.23	0.98	1.29	3.84	0.45	0.55	0.65	0.68	56.68	0.87	7.61	7.65
abs. error	[nm]	2.628E-03	2.288E-02	6.563E-03	9.581E-03	2.094E-02	4.108E-03	5.161E-03	6.944E-03	8.545E-03	1.093E+00	1.246E-02	1.396E-01	2.086E-01
FWHM	[uu]	0.62	0.54	0.67	0.74	0.55	0.91	0.94	1.07	1.26	1.93	1.43	1.84	2.73
rel. error	[%]	0.54	45.43	2.66	4.29	48.15	0.60	0.72	1.05	1.66	211.25	1.75	24.09	3791.95
abs. error	[a.u.]	317.00	451.09	322.96	102.23	334.84	101.63	135.47	160.58	238.46	68644.91	126.02	2898.51	1757.90
amplitude	[a.u.]	58197.90	992.91	12152.98	2383.45	695.40	16877.42	18701.47	15259.81	14323.97	32495.13	7200.65	12034.28	46.36
rel. error	[%]	9.135E-05	1.492E-03	1.229E-04	2.549E-04	1.435E-03	1.520E-04	1.809E-04	2.463E-04	3.337E-04	1.714E-02	6.109E-04	2.616E-03	2.850E-02
abs. error	[uu]	6.342E-04	1.036E-02	8.530E-04	1.770E-03	9.965E-03	1.056E-03	1.257E-03	1.711E-03	2.319E-03	1.192E-01	4.249E-03	1.820E-02	1.983E-01
peak pos.	[um]	694.23	694.26	694.26	694.37	694.33	694.58	694.73	694.87	695.05	695.31	695.52	695.78	695.86
voltage	[cV]	0	0	0	50	0	50	60	70	80	90	100	110	120
direction		down	down	dn										
error	[bar]	2.00	2.02	2.02	2.02	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06
oil P	[bar]	0	20	20	20	60	60	60	60	60	60	60	60	60

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error
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Qz P_calc
peak shift
rel. error
abs. error
FWHM
rel. error
abs. error
amplitude
rel. error
abs. error
peak pos.
voltage
direction
error
oil P

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Table

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error	[GPa]	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Qz P_calc	[GPa]	0.0000	0.1749	0.5759	0.3494	0.6252	0.5943	0.5668	0.4697	0.4163	0.3449	0.2501	0.1761	0.1246	0.1403	0.1906	0.1940	0.3065	0.3426
peak shift	[nm]	0.00	1.57	5.11	3.12	5.54	5.27	5.03	4.18	3.71	3.08	2.24	1.58	1.12	1.26	1.71	1.74	2.74	3.06
rel. error	[%]	10.15	1.33	3.39	1.41	4.18	1.96	2.04	2.32	2.10	2.14	2.27	2.47	2.29	2.69	2.92	2.83	3.05	1.45
abs. error	[uu]	1.428E+00	1.282E-01	3.435E-01	1.341E-01	4.271E-01	2.115E-01	2.403E-01	3.024E-01	3.184E-01	3.654E-01	4.400E-01	5.673E-01	6.585E-01	8.746E-01	1.027E+00	1.042E+00	1.171E+00	1.382E-01
FWHM	[uu]	14.07	9.66	10.13	9.50	10.23	10.77	11.77	13.05	15.15	17.06	19.36	22.98	28.77	32.55	35.18	36.83	38.41	9.50
rel. error	[%]	27.74	1.25	3.07	1.34	3.31	1.55	1.66	1.71	1.75	2.01	2.08	2.51	3.68	5.09	4.99	5.34	6.55	1.31
abs. error	[a.u.]	59.90	13.32	29.24	14.29	15.81	20.64	23.70	26.96	30.03	36.71	41.49	54.31	51.02	53.37	59.79	58.24	63.47	14.10
amplitude	[a.u.]	215.93	1065.03	951.76	1063.13	477.36	1328.07	1427.05	1578.31	1720.33	1823.62	1994.31	2159.51	1387.81	1047.96	1199.30	1091.22	969.52	1072.98
rel. error	[%]	0.10	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.03	0.04	0.06	0.07	0.07	0.08	0.01
abs. error	[uu]	4.741E-01	3.663E-02	9.609E-02	3.855E-02	1.122E-01	5.521E-02	6.300E-02	7.454E-02	8.167E-02	9.774E-02	1.136E-01	1.490E-01	2.014E-01	2.772E-01	3.053E-01	3.183E-01	3.724E-01	3.881E-02
peak pos.	[uu]	465.21	466.78	470.32	468.33	470.75	470.48	470.24	469.39	468.92	468.29	467.45	466.79	466.33	466.47	466.92	466.95	467.95	468.27
voltage	[cV]	0	0	50	0	60	70	80	100	110	120	130	140	150	160	165	170	175	180
direction		down	down	dn															
error	[bar]	2.00	2.02	2.05	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.06	2.07	2.07
oil P	[bar]	0	20	50	60	60	60	60	60	60	60	61	61	62	64	64	64	65	65

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Table 20

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[GPa]	0.0002	0.0002	0.0002	0.0002	0.0002	0.0003	0.0002	0.0002	0.0003	0.0003	0.0004	0.0005	0.0010	0.0018	0.0023		error	[GPa]	0.0809	0.0812	0.0817	0.0825	0.0843	0.0856	0.0813	0.0814	0.0816	0.0817	0.0821	0.0830	0.0840	0.0848
[GPa]	0.20	0.08	0.68	0.72	0.76	1.08	0.92	0.92	1.08	1.24	1.36	1.68	2.36	3.19	3.63		Rb P_calc	[GPa]	0.2696	0.6207	1.3523	2.0870	3.4287	4.2276	0.8913	1.0267	1.2166	1.3523	1.7873	2.5240	3.2638	0 701 0
[mm]	0.05	0.02	0.17	0.18	0.19	0.27	0.23	0.23	0.27	0.31	0.34	0.42	0.59	0.80	0.91		peak shift	[nm]	0.10	0.23	0.50	0.77	1.26	1.55	0.33	0.38	0.45	0.50	0.66	0.93	1.20	1 0 1
[%]	0.65	0.61	0.58	0.51	0.52	0.42	0.62	0.60	0.55	0.42	0.51	0.97	0.45	0.41	0.72		rel. error	[%]	2.15	2.94	0.54	0.59	0.80	1.26	2.00	1.05	1.32	0.96	0.76	2.87	0.73	1
[uu]	1.224E-03	1.251E-03	1.129E-03	1.043E-03	1.116E-03	9.318E-04	1.482E-03	1.190E-03	1.112E-03	8.478E-04	1.012E-03	1.965E-03	8.864E-04	1.108E-03	1.704E-03		abs. error	[um]	1.550E-02	2.249E-02	4.682E-03	6.556E-03	1.067E-02	1.373E-02	1.330E-02	6.861E-03	9.705E-03	7.240E-03	5.080E-03	2.222E-02	5.105E-03	
[uuu]	0.19	0.20	0.20	0.20	0.21	0.22	0.24	0.20	0.20	0.20	0.20	0.20	0.20	0.27	0.24		FWHM	[uu]	0.72	0.76	0.87	1.11	1.34	1.09	0.67	0.66	0.73	0.76	0.67	0.77	0.70	
[%]	0.85	0.73	0.73	0.63	0.61	0.47	0.96	0.78	0.73	0.53	0.67	1.20	0.57	0.49	0.84	004_PEB)	rel. error	[%]	2.49	4.24	0.76	0.83	2.15	2.47	2.97	1.06	1.71	1.44	0.78	4.50	0.80	0,0
[a.u.]	14.44	11.83	61.39	54.10	28.84	47.04	168.21	30.21	69.26	8.89	19.99	2.70	10.55	7.79	3.37	ts of ruby (	abs. error	[a.u.]	16.84	50.29	281.02	217.74	519.90	589.51	128.53	16.12	18.65	28.50	33.20	17.59	133.03	
[a.u.]	1693.87	1630.46	8442.37	8552.43	4712.21	9906.75	17563.04	3871.25	9454.11	1678.51	2974.83	224.85	1839.01	1603.65	401.36	itting resul	amplitude	[a.u.]	677.18	1186.64	36824.09	26273.10	24205.47	23848.30	4322.17	1516.02	1090.49	1983.95	4241.40	390.73	16686.06	
[%]	5.941E-05	5.815E-05	5.402E-05	4.938E-05	5.163E-05	4.256E-05	7.558E-05	5.763E-05	5.440E-05	4.068E-05	4.927E-05	9.347E-05	4.294E-05	5.092E-05	7.857E-05	Table 22: I	rel. error	[%]	4.995E-04	1.098E-03	1.626E-04	2.198E-04	4.583E-04	4.300E-04	3.670E-04	2.314E-04	3.316E-04	2.513E-04	1.842E-04	7.416E-04	1.794E-04	
[uu]	4.073E-04	3.986E-04	3.704E-04	3.385E-04	3.540E-04	2.918E-04	5.182E-04	3.951E-04	3.730E-04	2.790E-04	3.379E-04	6.411E-04	2.946E-04	3.494E-04	5.392E-04		abs. error	[uu]	3.468E-03	7.625E-03	1.130E-03	1.528E-03	3.188E-03	2.992E-03	2.549E-03	1.608E-03	2.304E-03	1.746E-03	1.280E-03	5.155E-03	1.248E-03	
[uu]	685.47	685.44	685.59	685.6	685.61	685.69	685.65	685.65	685.69	685.73	685.76	685.84	686.01	686.22	686.33		peak pos.	[uu]	694.33	694.46	694.73	695.00	695.49	695.78	694.56	694.61	694.68	694.73	694.89	695.16	695.43	00 100
[cV]	0	0	50	70	90	100	0	0	0	0	0	0	0	0	0		voltage	[cV]	0	0	50	70	60	100	0	0	0	0	0	0	0	
	down	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn	dn		direction		q	n	n	n	n	n	n	n	n	n	n	n	n	
[bar]	2.00	2.02	2.06	2.06	2.06	2.09	2.13	2.13	2.20	2.27	2.33	2.40	2.48	2.55	2.60		error	[bar]	2.00	2.02	2.06	2.06	2.06	2.09	2.13	2.20	2.27	2.33	2.40	2.48	2.55	0
[bar]	0	20	60	60	60	90	130	130	200	270	328	400	476	554	599		oil P	[bar]	0	20	60	60	60	06	130	200	270	328	400	476	554	
	[bar] [bar] [bar] [CV] [nm] [nm] [%] [a.u.] [a.u.] [%] [m] [nm] [%] [nm] [m] [m] [m] [GPa]	[bar]         [bar]         [cV]         [nm]         [nm]         [m]         [m]         [m]         [m]         [m]         [m]         [m]         [m]         [GPa]         [GPa]	[bar]         [bar]         [bar]         [rm]         [rm]	[bar]         [bar]         [bar]         [rm]         [rm]	[bar]         [bar]         [bar]         [rm]         [rm]	[bar]         [bar]         [rv]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [GPa]         [GPa] <td>[bar]         [bar]         [av]         [m]         [m]         [m]         [m]         [m]         [m]         [m]         [GPa]         [GPa]</td> <td>[bar][bar][au][rm][m][m][m][m][m][m][m][m][m][GPa][GPa]02.00down0685.474.073E-045.941E-051693.8714.440.850.191.224E-030.650.050.200.00022.00up0685.443.986E-045.815E-051630.4611.830.730.201.251E-030.650.050.00202.06up50685.593.704E-045.402E-058442.3761.390.730.201.129E-030.650.170.680.002602.06up70685.693.3704E-045.402E-058442.3754.100.630.201.129E-030.510.170.680.002602.06up90685.613.540E-045.163E-058552.4354.100.630.201.143E-030.510.180.720.002602.06up90685.613.540E-045.163E-058552.4354.100.610.211.116E-030.520.190.760.002602.09up100685.692.918E-045.163E-059906.7547.040.610.210.116E-030.220.190.760.00270685.692.918E-047.558E-059906.7547.040.610.210.1482E-030.271.080.003130100685.69<t< td=""><td>[bar][bar][rv][nm][nm][m][m][m][m][m][m][m][GPa][GPa]02.00down0685.474.073E-045.941E-051693.8714.440.850.191.224E-030.650.050.200.00022.00up0685.474.073E-045.815E-051630.4611.830.730.201.251E-030.610.020.0020.002602.06up70685.693.704E-045.402E-058442.3761.390.730.201.129E-030.510.170.680.002602.06up70685.613.540E-045.163E-058442.3754.100.630.201.129E-030.510.170.170.02602.06up70685.613.540E-045.163E-058442.3754.100.6630.201.143E-030.510.170.180.002602.06up90685.613.540E-045.163E-058712.2128.840.610.211.116E-030.520.190.760.002602.09100685.692.918E-045.163E-058712.2128.840.610.211.116E-030.520.190.760.002700685.692.918E-047.558E-059706.7547.040.470.229.318E-040.760.002130up0685.655.182E-04&lt;</td><td>[bar][bar][cv][nm][nn]</td><td>[bar][bar][cv][nm][nm][nm][nm][nm][nm][m][m][GPa][GPa][GPa]02.00down0685.474.073E.045.941E.05169.38714.440.850.191.224E.030.650.050.050.0002.00up0685.443.986E.045.815E.051630.4611.830.730.201.251E.030.610.020.060.0002.00up50685.593.704E.045.402E.058442.3761.390.730.201.129E.030.510.170.680.000602.06up70685.613.385E.045.402E.058442.3761.390.730.201.148E.030.510.170.680.000602.06up70685.613.540E.045.163E.05871.22128.840.610.211.148E.030.570.170.680.00090685.613.540E.045.163E.059906.7547.040.610.211.148E.030.570.190.760.0001302.13up0685.655.182E.047.558E.059906.7547.040.640.220.230.220.190.220.190.220.190.220.190.021302.13up0685.655.182E.047.558E.059906.7547.040.960.241.482E.030.620.230.92</td></t<><td>[bar][bar][cv][m][m][m][m][m][m][m][m][m][GPa][GPa][GPa]02.00down0685.474.073E-045.941E-05163.36714.440.850.191.224E-030.650.050.050.0002.00up0685.443.986E-045.815E-051630.4611.830.730.201.1251E-030.610.020.080.0002602.06up50685.593.704E-045.402E-058442.3761.390.730.201.129E-030.550.170.680.0002602.06up70685.613.385E-044.938E-058472.3761.390.730.201.148E-030.750.002602.06up70685.613.354E-045.163E-058472.3761.390.730.201.164E-030.750.002602.06up90685.613.546E-045.163E-058472.3761.390.730.201.168E-030.760.0002602.09up100685.653.518E-044.7326.1228.840.610.211.116E-030.270.190.760.0002700685.655.182E-047.558E-058906.7547.040.780.201.1482E-030.620.230.920.00021302.13up0685.655.182E-045.758E-058</td><td>[bar][bar][cv][nm][nm][nm][nm][nm][m][m][m][m][6Pa][6Pa]0.02.00down0685.474.073E.045.941E.051693.8714.440.850.191.224E.030.650.050.000.00022.00up0685.443.986E.045.815E.051630.4611.830.730.2011.29E.030.610.020.080.0022.00up50685.593.704E.045.492E.05844.3761.3990.730.2011.29E.030.610.070.08602.06up70685.613.385E.045.492E.05844.23754.100.630.2011.29E.030.750.0780.0002602.06up100685.613.540E.045.163E.058442.3754.100.630.2011.29E.030.750.0780.0021302.09up100685.613.540E.045.163E.05847.230.610.200.200.7280.0021302.13up00685.633.732E.045.758E.05387.125387.125387.1250.730.2010.920.200.200.921302.13up00685.633.732E.045.763E.05387.125387.125387.1250.730.2011.92E.030.600.230.920.9021302.13up</td><td></td><td></td><td></td><td>[par]         [par]         [cv]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [qpa]         [qpa]<td></td><td></td><td>Darl         Darl         Cold         Darl         <th< td=""><td></td><td></td><td></td><td></td><td>Deri         (ev)         (m)         (m)<!--</td--><td></td><td></td><td></td><td>Der         Der         C/V         Der         Der&lt;         Der&lt;         Der         Der         Der&lt;         Der&lt;</td><td></td><td></td><td></td></td></th<></td></td></td>	[bar]         [bar]         [av]         [m]         [m]         [m]         [m]         [m]         [m]         [m]         [GPa]         [GPa]	[bar][bar][au][rm][m][m][m][m][m][m][m][m][m][GPa][GPa]02.00down0685.474.073E-045.941E-051693.8714.440.850.191.224E-030.650.050.200.00022.00up0685.443.986E-045.815E-051630.4611.830.730.201.251E-030.650.050.00202.06up50685.593.704E-045.402E-058442.3761.390.730.201.129E-030.650.170.680.002602.06up70685.693.3704E-045.402E-058442.3754.100.630.201.129E-030.510.170.680.002602.06up90685.613.540E-045.163E-058552.4354.100.630.201.143E-030.510.180.720.002602.06up90685.613.540E-045.163E-058552.4354.100.610.211.116E-030.520.190.760.002602.09up100685.692.918E-045.163E-059906.7547.040.610.210.116E-030.220.190.760.00270685.692.918E-047.558E-059906.7547.040.610.210.1482E-030.271.080.003130100685.69 <t< td=""><td>[bar][bar][rv][nm][nm][m][m][m][m][m][m][m][GPa][GPa]02.00down0685.474.073E-045.941E-051693.8714.440.850.191.224E-030.650.050.200.00022.00up0685.474.073E-045.815E-051630.4611.830.730.201.251E-030.610.020.0020.002602.06up70685.693.704E-045.402E-058442.3761.390.730.201.129E-030.510.170.680.002602.06up70685.613.540E-045.163E-058442.3754.100.630.201.129E-030.510.170.170.02602.06up70685.613.540E-045.163E-058442.3754.100.6630.201.143E-030.510.170.180.002602.06up90685.613.540E-045.163E-058712.2128.840.610.211.116E-030.520.190.760.002602.09100685.692.918E-045.163E-058712.2128.840.610.211.116E-030.520.190.760.002700685.692.918E-047.558E-059706.7547.040.470.229.318E-040.760.002130up0685.655.182E-04&lt;</td><td>[bar][bar][cv][nm][nn]</td><td>[bar][bar][cv][nm][nm][nm][nm][nm][nm][m][m][GPa][GPa][GPa]02.00down0685.474.073E.045.941E.05169.38714.440.850.191.224E.030.650.050.050.0002.00up0685.443.986E.045.815E.051630.4611.830.730.201.251E.030.610.020.060.0002.00up50685.593.704E.045.402E.058442.3761.390.730.201.129E.030.510.170.680.000602.06up70685.613.385E.045.402E.058442.3761.390.730.201.148E.030.510.170.680.000602.06up70685.613.540E.045.163E.05871.22128.840.610.211.148E.030.570.170.680.00090685.613.540E.045.163E.059906.7547.040.610.211.148E.030.570.190.760.0001302.13up0685.655.182E.047.558E.059906.7547.040.640.220.230.220.190.220.190.220.190.220.190.021302.13up0685.655.182E.047.558E.059906.7547.040.960.241.482E.030.620.230.92</td></t<> <td>[bar][bar][cv][m][m][m][m][m][m][m][m][m][GPa][GPa][GPa]02.00down0685.474.073E-045.941E-05163.36714.440.850.191.224E-030.650.050.050.0002.00up0685.443.986E-045.815E-051630.4611.830.730.201.1251E-030.610.020.080.0002602.06up50685.593.704E-045.402E-058442.3761.390.730.201.129E-030.550.170.680.0002602.06up70685.613.385E-044.938E-058472.3761.390.730.201.148E-030.750.002602.06up70685.613.354E-045.163E-058472.3761.390.730.201.164E-030.750.002602.06up90685.613.546E-045.163E-058472.3761.390.730.201.168E-030.760.0002602.09up100685.653.518E-044.7326.1228.840.610.211.116E-030.270.190.760.0002700685.655.182E-047.558E-058906.7547.040.780.201.1482E-030.620.230.920.00021302.13up0685.655.182E-045.758E-058</td> <td>[bar][bar][cv][nm][nm][nm][nm][nm][m][m][m][m][6Pa][6Pa]0.02.00down0685.474.073E.045.941E.051693.8714.440.850.191.224E.030.650.050.000.00022.00up0685.443.986E.045.815E.051630.4611.830.730.2011.29E.030.610.020.080.0022.00up50685.593.704E.045.492E.05844.3761.3990.730.2011.29E.030.610.070.08602.06up70685.613.385E.045.492E.05844.23754.100.630.2011.29E.030.750.0780.0002602.06up100685.613.540E.045.163E.058442.3754.100.630.2011.29E.030.750.0780.0021302.09up100685.613.540E.045.163E.05847.230.610.200.200.7280.0021302.13up00685.633.732E.045.758E.05387.125387.125387.1250.730.2010.920.200.200.921302.13up00685.633.732E.045.763E.05387.125387.125387.1250.730.2011.92E.030.600.230.920.9021302.13up</td> <td></td> <td></td> <td></td> <td>[par]         [par]         [cv]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [qpa]         [qpa]<td></td><td></td><td>Darl         Darl         Cold         Darl         <th< td=""><td></td><td></td><td></td><td></td><td>Deri         (ev)         (m)         (m)<!--</td--><td></td><td></td><td></td><td>Der         Der         C/V         Der         Der&lt;         Der&lt;         Der         Der         Der&lt;         Der&lt;</td><td></td><td></td><td></td></td></th<></td></td>	[bar][bar][rv][nm][nm][m][m][m][m][m][m][m][GPa][GPa]02.00down0685.474.073E-045.941E-051693.8714.440.850.191.224E-030.650.050.200.00022.00up0685.474.073E-045.815E-051630.4611.830.730.201.251E-030.610.020.0020.002602.06up70685.693.704E-045.402E-058442.3761.390.730.201.129E-030.510.170.680.002602.06up70685.613.540E-045.163E-058442.3754.100.630.201.129E-030.510.170.170.02602.06up70685.613.540E-045.163E-058442.3754.100.6630.201.143E-030.510.170.180.002602.06up90685.613.540E-045.163E-058712.2128.840.610.211.116E-030.520.190.760.002602.09100685.692.918E-045.163E-058712.2128.840.610.211.116E-030.520.190.760.002700685.692.918E-047.558E-059706.7547.040.470.229.318E-040.760.002130up0685.655.182E-04<	[bar][bar][cv][nm][nn]	[bar][bar][cv][nm][nm][nm][nm][nm][nm][m][m][GPa][GPa][GPa]02.00down0685.474.073E.045.941E.05169.38714.440.850.191.224E.030.650.050.050.0002.00up0685.443.986E.045.815E.051630.4611.830.730.201.251E.030.610.020.060.0002.00up50685.593.704E.045.402E.058442.3761.390.730.201.129E.030.510.170.680.000602.06up70685.613.385E.045.402E.058442.3761.390.730.201.148E.030.510.170.680.000602.06up70685.613.540E.045.163E.05871.22128.840.610.211.148E.030.570.170.680.00090685.613.540E.045.163E.059906.7547.040.610.211.148E.030.570.190.760.0001302.13up0685.655.182E.047.558E.059906.7547.040.640.220.230.220.190.220.190.220.190.220.190.021302.13up0685.655.182E.047.558E.059906.7547.040.960.241.482E.030.620.230.92	[bar][bar][cv][m][m][m][m][m][m][m][m][m][GPa][GPa][GPa]02.00down0685.474.073E-045.941E-05163.36714.440.850.191.224E-030.650.050.050.0002.00up0685.443.986E-045.815E-051630.4611.830.730.201.1251E-030.610.020.080.0002602.06up50685.593.704E-045.402E-058442.3761.390.730.201.129E-030.550.170.680.0002602.06up70685.613.385E-044.938E-058472.3761.390.730.201.148E-030.750.002602.06up70685.613.354E-045.163E-058472.3761.390.730.201.164E-030.750.002602.06up90685.613.546E-045.163E-058472.3761.390.730.201.168E-030.760.0002602.09up100685.653.518E-044.7326.1228.840.610.211.116E-030.270.190.760.0002700685.655.182E-047.558E-058906.7547.040.780.201.1482E-030.620.230.920.00021302.13up0685.655.182E-045.758E-058	[bar][bar][cv][nm][nm][nm][nm][nm][m][m][m][m][6Pa][6Pa]0.02.00down0685.474.073E.045.941E.051693.8714.440.850.191.224E.030.650.050.000.00022.00up0685.443.986E.045.815E.051630.4611.830.730.2011.29E.030.610.020.080.0022.00up50685.593.704E.045.492E.05844.3761.3990.730.2011.29E.030.610.070.08602.06up70685.613.385E.045.492E.05844.23754.100.630.2011.29E.030.750.0780.0002602.06up100685.613.540E.045.163E.058442.3754.100.630.2011.29E.030.750.0780.0021302.09up100685.613.540E.045.163E.05847.230.610.200.200.7280.0021302.13up00685.633.732E.045.758E.05387.125387.125387.1250.730.2010.920.200.200.921302.13up00685.633.732E.045.763E.05387.125387.125387.1250.730.2011.92E.030.600.230.920.9021302.13up				[par]         [par]         [cv]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [nm]         [qpa]         [qpa] <td></td> <td></td> <td>Darl         Darl         Cold         Darl         <th< td=""><td></td><td></td><td></td><td></td><td>Deri         (ev)         (m)         (m)<!--</td--><td></td><td></td><td></td><td>Der         Der         C/V         Der         Der&lt;         Der&lt;         Der         Der         Der&lt;         Der&lt;</td><td></td><td></td><td></td></td></th<></td>			Darl         Darl         Cold         Darl         Darl <th< td=""><td></td><td></td><td></td><td></td><td>Deri         (ev)         (m)         (m)<!--</td--><td></td><td></td><td></td><td>Der         Der         C/V         Der         Der&lt;         Der&lt;         Der         Der         Der&lt;         Der&lt;</td><td></td><td></td><td></td></td></th<>					Deri         (ev)         (m)         (m) </td <td></td> <td></td> <td></td> <td>Der         Der         C/V         Der         Der&lt;         Der&lt;         Der         Der         Der&lt;         Der&lt;</td> <td></td> <td></td> <td></td>				Der         Der         C/V         Der         Der<         Der<         Der         Der         Der<         Der<			

 Table 21: Fitting results of strontium borate (004 PEB)

error	[GPa]	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Qz P_calc	[GPa]	0.2986	0.8762	1.0411	1.3584	1.5383	2.1731	2.8685	3.2211
peak shift	[uu]	2.67	7.71	9.12	11.80	13.30	18.49	24.00	26.73
rel. error	[%]	14.69	12.90	17.33	20.71	3.33	5.64	4.16	4.80
abs. error	[uu]	2.092E+00	1.442E+00	2.294E+00	3.947E+00	3.089E-01	5.203E-01	3.873E-01	4.146E-01
FWHM	[nm]	14.24	11.17	13.24	19.06	9.28	9.23	9.32	8.64
rel. error	[%]	11.09	23.39	12.81	23.51	2.97	5.05	3.09	4.87
abs. error	[a.u.]	63.74	35.00	51.28	68.26	27.86	26.80	27.77	21.76
amplitude	[a.u.]	574.55	149.64	400.42	290.36	937.23	530.37	898.23	446.51
rel. error	[%]	0.11	0.11	0.12	0.24	0.02	0.03	0.02	0.03
abs. error	[um]	5.157E-01	5.234E-01	5.656E-01	1.132E+00	8.647E-02	1.458E-01	9.907E-02	1.230E-01
peak pos.	[uu]	467.88	472.92	474.33	477.01	478.51	483.70	489.21	491.94
voltage	[cV]	0	0	0	0	0	0	0	0
direction		q	n	n	n	n	n	n	n
error	[bar]	2.01	2.13	2.20	2.27	2.40	2.48	2.55	2.60
oil P	[bar]	5	130	200	270	400	476	554	603

Table 23: Fitting results of quartz (004\_PEB)

experiment	confining gasket	middle gasket	inner gasket	oven	graphite ring	sample chamber
001_PEA_DF	PEEK 450g	1	NaCl	Steel tube	angular ring	pyrophyllite sheathed K-type
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 4.00 mm,	OD: 5.0 mm	thermocouple
	ID: 9.9 mm,		ID: 4.1 mm,	ID: 3.70 mm,	ID: 4.0 mm	
	h: 3.3 mm		h: 4.0 mm	h: 3.0 mm	h: 2 mm	
002_PEA_DF	PEEK 450g		NaCl	steel tube	OD: 5.0 mm	alumina sheathed K-type
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 4.00 mm,	ID: 4.0 mm	thermocouple in alumina tube
	ID: 9.9 mm,		ID: 4.1 mm,	ID: 3.70 mm,	h: 1 mm	
	h: 3.3 mm		h: 4.0 mm	h: 3.0 mm		
003_PEA_DF	PEEK 450g		NaCl	steel tube	OD: 5.0 mm	alumina sheathed K-type
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 4.00 mm,	ID: 4.0 mm	thermocouple in alumina tube
	ID: 9.9 mm,		ID: 4.1 mm	ID: 3.70 mm,	h:1 mm	
	h: 3.3 mm		h: 4.0 mm	h: 3.0 mm		
004_PEA_DFSC	PEEK 450g	1	NaCl	steel tube	OD: 4.0 mm	glass (OD: 3.0 mm, h: 1.5 mm)
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 4.00 mm,	ID: 3.2 mm	inner salt powder $(2\% H_2 O)$
	ID: 9.9 mm,		ID: 4.1 mm,	ID: 3.70 mm,	h: 1.0 mm	sample:
	h: 3.3 mm		h: 4.0 mm	h: 3.5 mm		- SrB <sub>4</sub> O <sub>7</sub> :Sm <sup>2+</sup> powder (2 knife tips)
						- ruby (1 mm)
005_PEA_DFSC	PEEK 450g	ı	NaCl	Inconel tube		glass (OD: 3.0 mm, h:1.5 mm)
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 3.7 mm,		inner salt powder $(5\% H_2 O)$
	ID: 9.9 mm,		ID: 3.8 mm	ID: 3.5 mm,		sample:
	h: 3.3 mm)		h: 4.0 mm	h: 3.5 mm		- SrB <sub>4</sub> O <sub>7</sub> :Sm <sup>2+</sup> powder (2 knife tips)
						- ruby (1 mm)
006_PEA_DFSC	PEEK 450g	1	NaCl	Inconel tube	OD: 4.0 mm	glass (OD: 3.0 mm, h:1.5 mm)
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 3.7 mm,	ID: 3.7 mm	inner salt powder $(3\% H_2 O)$
	ID: 9.9 mm,		ID: 3.8 mm	ID: 3.5 mm,	h: 1.0 mm	sample:
	h: 3.3 mm		h: 4.0 mm	h: 4.7 mm		- $SrB_4O_7$ : $Sm^{2+}$ powder (4 knife tips)
						- ruby (1.5 mm)

Table 24: Overview of high-temperature experiments. (part 1)

		Table 25: Overview of	nigh-temperature	experiments. (p	art 2)		
experiment	confining gasket	middle gasket	inner gasket	oven	graphite ring	sample chamber	
007_PEA_DFSC	CuBe	I	NaCl	Inconel tube	OD: 4.0 mm	glass (OD: 3.0 mm, h: 1.5 mm)	
	UD: 9.9 mm.		UD: 3.8 mm.	UD: 3.5 mm.	h: 1.0 mm	sample:	
	h: 1.2 mm		h1: 4.0 mm,	h: 4.7 mm		- SrB <sub>4</sub> O <sub>7</sub> :Sm <sup>2+</sup> powder (4 knife tips)	
	2 Muscovite disks		h2: 3.5 mm			- ruby (1.5 mm)	
	OD: 16.0 mm,						
	ID: 9.9 mm, h: 0.6 mm						
	h: 0.6 mm						
008_PEA_SCAB	Steel (INOX 1.4571)		NaCl	Inconel tube	OD 4.0 mm	glass (OD: 3.0 mm, h: 1.5 mm)	
	OD: 15.0 mm,		OD: 9.8 mm,	OD: 3.7 mm,	ID 3.7 mm	inner salt powder $(3\% H_2O)$	
	ID: 9.9 mm,		ID: 3.5 mm,	ID: 3.5 mm,	h: 1.0 mm	sample:	
	h: 1.2 mm		h1: 4.0 mm,	h: 6.0 mm	37° internal angle	- $SrB_4O_7$ : $Sm^{2+}$ powder (4 knife tips)	
	1 Muscovite disks		h2: 2.6 mm			ruby (1.5 mm)	
	OD: 16.0 mm,						
	ID: 9.9 mm,						
	h: 0.3 mm						
009_PEA_DFSC	CuBe	pyrophyllite	NaCl	Inconel tube	OD: 4.0 mm	glass (0: 3.0 mm, h: 1.5 mm)	
	OD: 15.0 mm,	(fired at 1273 K)	OD: 7.0 mm,	OD: 3.7 mm;	ID: 3.7 mm	inner salt powder $(3\% H_2O)$	
	ID: 9.9 mm,	OD: 9.8 mm,	ID: 3.5 mm,	ID: 3.5 mm,	h: 1.0 mm	sample:	
	h: 1.2 mm	ID: 7.5 mm,	h1: 4.0 mm,	h: 5.5 mm	40° internal angle	- $SrB_4O_7$ : $Sm^{2+}$ powder (4 knife tips)	
	MgO glue	h: 1.8 mm	h2: 2.1 mm			- ruby (1.5 mm)	
	h: 0.3 mm					Ag pieces	
010_PEA_SCDF	CuBe	pyrophyllite	NaCl	Inconel tube	OD: 4.0 mm	alumina sheathed K-type	
	OD: 15.0 mm,	(fired at 1223 K for 3h)	OD: 7.0 mm,	OD: 3.7 mm,	ID: 3.7 mm	thermocouple in alumina tube	
	ID: 9.9 mm,	OD: 9.8 mm,	ID: 3.5 mm,	ID: 3.5 mm,	h: 0.8 mm	glass (0: 3.0 mm, h: 1.5 mm)	
	h: 1.2 mm	ID: 7.0 mm,	h1: 4.0 mm,	h: 5.5 mm	40° internal angle	inner salt powder (3% $H_2O$ )	А
	MgO glue	h: 2.0 mm	h2: 2.0 mm			sample:	ppe
	h: 0.3 mm					- $SrB_4O_7$ :Sm <sup>2+</sup> powder (4 knife tips)	endi
						- rudy () - ×	Х

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experiment	confining gasket	middle gasket	inner gasket	oven	graphite ring	sample chamber
002_PEB	CuBe	pyrophyllite	NaCl	Inconel tube	OD: 4.0 mm	glass (OD: 3.0 mm, h:1.5 mm)
	OD: 15.0 mm,	(fired at 1223 K for 3h)	OD: 7.0 mm,	OD: 3.7 mm,	O 3.8 mm	inner salt powder $(3\% \text{ distilled H}_2\text{O})$
	ID: 9.9 mm,	OD: 9.8 mm,	ID: 3.5 mm,	ID: 3.5 mm,	h: 0.8 mm	sample:
	h: 1.2 mm	ID: 7.0 mm,	h1: 4.3 mm,	h: 5.5 mm	40° internal angle	- SrB <sub>4</sub> O <sub>7</sub> :Sm <sup>2+</sup> powder (4 knife tips)
	MgO glue	h: 2.0 mm	h2: 2.0 mm			ruby (1.5 mm)
	h: 0.3 mm					
003_PEB	CuBe	pyrophyllite	NaCl	Inconel tube	O 4.0 mm	inner salt powder $(3\% H_2 O)$
	OD: 15.0 mm,	(fired at 1223 K for 3h)	OD: 7.0 mm,	OD: 3.7 mm,	OD: 3.8 mm	sample:
	ID: 9.9 mm,	OD: 9.8 mm,	ID: 3.5 mm,	ID: 3.5 mm,	h: 0.8 mm	- SrB <sub>4</sub> O <sub>7</sub> :Sm <sup>2+</sup> powder (4 knife tips)
	h: 1.2 mm	ID: 7.0 mm,	h1: 4.0 mm,	h: 5.5 mm	40° internal angle	ruby (1.5 mm)
	MgO glue	h: 2.0 mm	h2: 2.0 mm			
	h: 0.3 mm					
004_PEB	CuBe	pyrophyllite	NaCl	Inconel tube	OD: 4.0 mm	inner salt powder (3% H <sub>2</sub> O
	OD: 15.0 mm,	(fired at 1223 K for 3h)	OD: 7.0 mm,	OD; 3.7 mm	ID: 3.8 mm	sample:
	ID: 9.9 mm,	OD: 9.8 mm,	ID: 3.7 mm,	ID: 3.5 mm,	h: 0.8 mm	- SrB <sub>4</sub> O <sub>7</sub> :Sm <sup>2+</sup> powder (4 knife tips)
	h: 1.2 mm	ID: 7.0 mm,	h1: 4.0 mm,	h: 5.6 mm	40° internal angle	-ruby (1.5 mm)
	MgO glue	h: 2.0 mm	h2: 2.0 mm			
	h: 0.3 mm					

Table 26: Overview of high-temperature experiments. (part 3)

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oil pressure [bar] /	measurement time of	measurement time	measurement time
voltage [V]	strontium borate [s]	of ruby [s]	of quartz [s]
14	10 (2*5)	10 (2*5)	90 (3*30)
40	10 (2*5)	10 (2*5)	/
48	90 (3*30)	90 (3*30)	
48 / 0.3	90 (3*30)	90 (3*30)	180 (3*60)
48 / 1.0	90 (3*30)	90 (3*30)	180 (3*60)
60	10 (2*5)	10 (2*5)	180 (3*60)
60 / 0.25	10 (2*5 )	10 (2*5)	180 (3*60)
60 / 0.50	10 (2*5)	10 (2*5)	180 (3*60)
61 / 0.75	10 (2*5)	10 (2*5)	120 (3*40)
61 / 1.0	10 (2*5)	10 (2*5 )	180 (3*60)
75 / 1.0	90 (3*30)	90 (3*30)	240 (3*80)
89 / 1.0	90 (3*30)	90 (3*30)	180 (3*60)
135	90 (3*30)	90 (3*30)	180 (3*60)
198	60 (3*20)	60 (3*20)	120 (2*60)
270	60 (3*20)	60 (3*20)	120 (2*60)
333	60 (3*20)	60 (3*20)	120 (2*60)
409	60 (3*20)	60 (3*20)	120 (2*60)
417	60 (3*20)	60 (3*20)	120 (2*60)
466	60 (3*20)	60 (3*20)	30 (2*15)
480	60 (3*20)	60 (3*20)	30 (2*15)
560	15/30	15/30	30 (2*15)
593	15 (3*5)	15 (3*5)	30 (2*15)
600	15 (3*5)	15 (3*5)	180 (3*60)
502_d	15 (3*5)	15 (3*5)	180 (3*60)
499_d	15 (3*5)	15 (3*5)	180 (3*60)
401_d	15 (3*5)	15 (3*5)	180 (3*60)
397_d	15 (3*5)	15 (3*5)	180 (3*60)
301_d	15 (3*5)	15 (3*5)	180 (3*60)
296_d	15 (3*5)	15 (3*5)	180 (3*60)
204_d	15 (3*5)	15 (3*5)	90 (3*30)
200_d	15 (3*5)	15 (3*5)	90 (3*30)
105_d	3 (3*1)	3 (3*1)	60 (2*15)
101_d	15 (3*5)	15 (3*5)	60 (2*15)
95 d	15 (3*5)	15 (3*5)	60 (2*15)

**Table 27:** Integration time of fluorescence and Raman measurement for each pressure change of experimentwith glass window ( $002\_PEB$ ).

oil pressure [bar] /	measurement time of	measurement time	measurement time
voltage [V]	strontium borate [s]	of ruby [s]	of quartz [s]
20	15 (3*5)	9 (3*3)	60 (3*20)
20 / 0.5	9 (3*3)	9 (3*3)	60 (3*20)
60 / 0.0	32 (4*8)	32 (4*8)	120 (4*30)
60 / 0.5	9 (3*3)	9 (3*3)	120 (4*30)
60 / 0.6	12 (4*3)	12 (4*3)	120 (4*30)
60 / 0.7	12 (4*3)	12 (4*3)	120 (4*30)
60 / 0.8	12 (4*3)	12 (4*3)	120 (4*30)
60 / 0.9	12 (4*3)	12 (4*3)	120 (4*30)
60 / 1.0	12 (4*3)	12 (4*3)	120 (4*30)
60 / 1.1	12 (4*3)	12 (4*3)	120 (4*30)
60 / 1.2	12 (4*3)	12 (4*3)	120 (4*30)
61 / 1.3	12 (4*3)	12 (4*3)	120 (4*30)
61 / 1.4	12 (4*3)	12 (4*3)	120 (4*30)
62 / 1.5	12 (4*3)	12 (4*3)	120 (4*30)
64 / 1.6	32 (4*8)	32 (4*8)	120 (4*30)
64 / 1.7	32 (4*8)	32 (4*8)	120 (4*30)
64 / 1.8	/	/	120 (4*30)
20_d	32 (4*8)	32 (4*8)	120 (4* 30)
0_d	8 (4*2)	1 (3*0.2)	120 (4* 30)

**Table 28:** Integration time of fluorescence and Raman measurement for each pressure change of experiment without glass window (003\_PEB).

**Table 29:** Integration time of fluorescence and Raman measurement for each pressure change of experiment without glass window (004\_PEB).

oil pressure [bar]/	measurement time of	measurement time
voltage [V]	strontium borate and ruby[s]	of quartz [s]
0_d	24 (3*8)	90 (3*30)
20	12 (3*4)	90 (3*30)
60 / 0.5	32 (4*8)	120 (4*30)
60 / 0.7	32 (4*8)	120 (4*30)
60 / 0.9	32 (4*8)	120 (4*30)
90 / 1.0	32 (4*8)	120 (4*30)
130	32 (4*8)	120 (4*30)
200	32 (4*8)	120 (4*30)
270	32 (4*8)	120 (4*30)
328	32 (4*8)	120 (4*30)
400	32 (4*8)	90 (3*30)
476	32 (4*8)	90 (3*30)
554	32 (4*8)	90 (3*30)
599	32 (4*8)	90 (3*30)