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# Structural phase transition in $\text{ZrO}_2$ induced by swift heavy ion irradiation at high pressure

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## Abstract

Exposing pressurized crystals to GeV heavy ions reveals unexpected structural changes. Irradiated at ambient conditions, natural zirconia ( $\text{ZrO}_2$ ) transforms from the monoclinic structure to its tetragonal (high-temperature) phase. For this process the required fluence must exceed  $5 \times 10^{12}$  ions/cm<sup>2</sup> for Pb and U, and become even significantly higher for lighter ions. If samples are pressurized during irradiation using diamond anvil cells, the required fluence drops at least by one order of magnitude. The efficiency of the monoclinic to tetragonal phase transition becomes larger with increasing pressure.

**Keywords:** Zirconia, phase transition, high pressure, irradiation effect, Raman spectroscopy

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# 1 Introduction

The initial motivation in combining high-pressure and irradiation with swift heavy ions has its origin in geophysics, where fission tracks are analyzed for dating purposes [1][2]. Also in materials science, the question how solids respond to the simultaneous exposure to pressure and extreme energy input has raised large interest [3]. The creation of new phases otherwise not accessible may become possible for manufacturing novel substances with particular characteristics. In this study, we are concentrating on zirconia, which is known for its thermal and mechanical resistance and its radiation hardness. Because of these properties,  $\text{ZrO}_2$  is often used as inert fuel matrix in nuclear reactors [4] [5] or as a container for radioactive e.g. plutonium waste [6].

At ambient temperature and pressure conditions,  $\text{ZrO}_2$  is a white powder with a monoclinic structure.  $\text{ZrO}_2$  has two known high-pressure polymorphs (orthorhombic I and orthorhombic II [7]) and two different high-temperature polymorphs (tetragonal and cubic) (see Fig 1).

At about  $1200^\circ\text{C}$ , a martensitic-type phase transition occurs to a tetragonal derivative of the fluorite structure, and at around  $2400^\circ\text{C}$  another structural phase transition leads to a true cubic fluorite structure that is stable up to the melting temperature of  $\sim 2700^\circ\text{C}$  [8]. These high-temperature phases cannot be quenched, but they can be stabilized at room temperature by replacing up to 15% of Zr with larger cations (e.g. La, Mg, Y) [9]. Stoichiometric as well as stabilized zirconia has previously been irradiated with a wide spectrum of energetic particles in the nuclear [10][11][12][13] and electronic stopping regime [8][14][15]. Both compound shows a remarkable resistance against amorphization if the grain size is not on the nm scale [16]. The polymorphism of zirconia plays an important role for the evolution of the radiation damage.  $\text{ZrO}_2$  is one of the few materials that undergoes, instead of amorphization, a crystalline-crystalline (displacive) phase transition to the higher symmetry phase, i.e. monoclinic  $\text{ZrO}_2$  transforms either to the tetragonal or the cubic structure. Once this has occurred, the new crystalline phase persists without further transitions as observed e.g.

with 800-keV Bi ions dominated by nuclear stopping [12] and with various swift heavy ions for which the electronic stopping exceeded 13 keV/nm [17][8][18][19]. However, even at high fluences, the transformation into the tetragonal polymorph is not complete but saturates below 100% [17]. In contrast to tetragonal ZrO<sub>2</sub> created by heating, the radiation induced tetragonal phase does not return to the monoclinic form. Including pressure as an additional parameter, new aspects of the structural transformations can be investigated.

## 2 Experimental

For pressurization of samples, Diamond Anvil Cells (DAC) of the Merrill-Bassett type [20] were used. Several grains (size  $\sim 0.2 \mu\text{m}$ ) of monoclinic ZrO<sub>2</sub> powder (from Goodfellow company) were inserted in the central aperture (diameter of 150  $\mu\text{m}$ ) of a stainless steel gasket mounted between two diamonds each with a culet face with a diameter of 600  $\mu\text{m}$  and a thickness of 2.64 mm. In addition, the sample chamber was filled with a 16:3:1 mixture of methanol:ethanol:water as optically transparent pressure medium to insure hydrostatic conditions [21]. Pressure was applied by squeezing the gasket by two diamonds up to a pressure between 4.3 and 13.4 GPa. The pressure was measured by adding a small ruby crystal into the sample chamber and measuring the wavelength of the red fluorescence line [22]. The pressurized ZrO<sub>2</sub> samples embedded in the DAC were exposed to relativistic ions from the SIS heavy-ion synchrotron of GSI (Darmstadt). The experiments were performed at room temperature using either <sup>238</sup>U or <sup>208</sup>Pb ions with kinetic energies of about 200 MeV per nucleon (MeV/u) (see Table 1).

The energy is high enough so that the ions traverse the first diamond and the entire sample (Fig 2). Moreover, the energy loss inside the sample is close to the Bragg maximum. Details of the irradiation parameters are summarized in Table 1. The irradiation experiment at the SIS was performed with a pulsed beam of 0.3 spills/s (extraction time of each spill  $\sim 1.4$  seconds) containing

about  $\sim 2\text{-}5\times 10^8$  ions/cm<sup>2</sup> per spill. The flux was monitored via a calibrated secondary-electron emitting detector (SEETRAM) [23]. The fluence applied ranged between 1 and  $2.5\times 10^{11}$  ions/cm<sup>2</sup>. Fluence cross-checks were performed by counting tracks in an irradiated mica sample inspected by atomic force microscopy [24]. As reference, an additional ZrO<sub>2</sub> sample was irradiated behind a diamond applying identical conditions, but without external pressure. At the SIS, the beamtime and thus possible maximum fluences are limited therefore we performed additional reference irradiations to test radiation effects at high fluences (fluence series of  $5\times 10^{10}$  to  $5\times 10^{12}$  ions/cm<sup>2</sup>) with <sup>238</sup>U and <sup>208</sup>Pb ions at the UNILAC (Universal Linear Accelerator) of GSI. Because the maximum available energy at the UNLIAC is only 11.1 MeV/u (corresponding to a range of  $\sim 60$   $\mu$ m for U-ions), the ZrO<sub>2</sub> samples were irradiated without using the DAC. The energy loss was 42 keV/nm for <sup>208</sup>Pb and 53 keV/nm for <sup>238</sup>U, respectively. Both values are well above the threshold of 13 keV/nm necessary for a transformation from the monoclinic to the tetragonal phase [8]. After irradiation, the samples were analyzed by confocal Raman spectroscopy using a HR800-180° system (Horiba Jobin Yvon) with a 20 mW He-Ne-Laser and an excitation wavelength of 632.8 nm.

### 3 Results and Discussion

The Raman spectra of ZrO<sub>2</sub> before and after irradiation with <sup>208</sup>Pb ions at the UNILAC are displayed in Fig. 3. Up to a fluence of  $1\times 10^{12}$  ions/cm<sup>2</sup> for Pb as well as U, the Raman spectra hardly change and predominantly show the bands typical of monoclinic ZrO<sub>2</sub> at 180, 190, 334, 348, 380, 476, 617, and 638 cm<sup>-1</sup> [13][25]. At fluences around  $2\times 10^{12}$  ions/cm<sup>2</sup>, small modifications become visible. At  $5\times 10^{12}$  ions/cm<sup>2</sup> and above, the spectra exhibit new broad bands located at 148, 260, 465, and 640 cm<sup>-1</sup> which are assigned to the tetragonal phase of ZrO<sub>2</sub> [8][25][26]. For both ion species, this transformation occurs in a rather small fluence regime between  $2\times 10^{12}$  and  $5\times 10^{12}$  ions/cm<sup>2</sup>. Further

fluence increase to  $7.5 \times 10^{12}$  Pb-ions/cm<sup>2</sup> does not induce additional changes. This effect is similar to the observations made earlier by Benyagoub for Ni (135 MeV) and Kr (300 MeV) ions [27], but saturation for these lighter ions requires fluences higher than  $2.5 \times 10^{13}$  ions/cm<sup>2</sup>. Also in agreement with [27], Pb- or U-irradiated ZrO<sub>2</sub> does not fully transform into its tetragonal phase but still exhibits some Raman bands of the monoclinic phase (e.g. at 180 and 190 cm<sup>-1</sup>.)

The samples irradiated at high pressure show quite different results. In a first approach, Raman spectra of irradiated ZrO<sub>2</sub> samples still pressurized in the DAC to 10.9 GPa were recorded, but the quality of the spectra is quite poor, because the Raman light has to pass the diamond twice before reaching the detector. Therefore, the intensity of the signal is extremely weak, and the background increases enormously so that recording a single spectrum may take several hours. In the few spectra collected, no significant change could be observed, which was not too surprising given the low fluences available for the DAC irradiation. Another complication for a comparative study resulted from the fact that at a pressure of 10.9 GPa, the ZrO<sub>2</sub> sample is no longer monoclinic but has transformed to its high-pressure orthorhombic I phase.

The Raman investigations concentrated on samples removed from the DAC, i.e. at ambient conditions. With the mapping function, several areas of the sample were examined using the microscope objective with the largest magnification (100x) with a spatial resolution of about 1 μm.

Surprisingly, the Raman spectra varied strongly with the position where the spectrum was acquired. Fig. 4 shows four representative Raman spectra of the sample irradiated with  $2.5 \times 10^{11}$  Pb-ions/cm<sup>2</sup> at 10.9 GPa. Spectrum (a) resembles that of an unirradiated monoclinic ZrO<sub>2</sub> sample and was found at about 50% of the tested sample areas. Spectrum (b) is dominated by deformed monoclinic ZrO<sub>2</sub> bands with a small trace of tetragonal ZrO<sub>2</sub> indicated by bands at 148 and 260 cm<sup>-1</sup>. Spectrum (c) shows a mixture of monoclinic and tetragonal ZrO<sub>2</sub> while spectrum (d) resembles that of almost pure tetragonal ZrO<sub>2</sub>. A nearly complete transformation appeared at about 7% of the tested sample

areas while all other spectra showed different mixtures of monoclinic and tetragonal  $\text{ZrO}_2$ . Comparing the relative intensities of the monoclinic bands at 180 and  $190 \text{ cm}^{-1}$  and the tetragonal band at  $148 \text{ cm}^{-1}$ , the amount of monoclinic  $\text{ZrO}_2$  ( $X_m$ ) in the two-phase mixture can be estimated from the intensities of the monoclinic ( $I_m$ ) and tetragonal ( $I_t$ ) bands [25].

$$X_m = \frac{I_m(180 \text{ cm}^{-1}) + I_m(190 \text{ cm}^{-1})}{I_m(180 \text{ cm}^{-1}) + I_m(190 \text{ cm}^{-1}) + I_t(148 \text{ cm}^{-1})} \quad (1)$$

Eq. (1) yields  $X_m = 99\%$  for spectrum 4a,  $X_m = 97\%$  for 4b,  $X_m = 70\%$  for 4c, and  $X_m = 13\%$  for 4d. This significantly exceeds the tetragonal content of the sample irradiated with  $7.5 \times 10^{12}$  Pb-ions/ $\text{cm}^2$  at the UNILAC where the amount of monoclinic  $\text{ZrO}_2$  did not surpass 28%.

To exclude that pressure alone could have caused this strong transformation, a reference sample was pressurized to 11 GPa remaining in the DAC for two weeks. A second reference sample which was irradiated through a single diamond without being pressurized was also analyzed. The Raman spectra of both reference samples showed no deviation from a virgin sample (see Fig 5).

To determine the effect of pressure,  $\text{ZrO}_2$  samples were irradiated at various pressures (ambient, 4.3, 7.6, 11.1, and 13.6 GPa) while keeping energy and fluence ( $1.5 \times 10^{11}$  U-ions/ $\text{cm}^2$ ) constant (see Table 1). As stated before, the transformation of the sample is not homogeneously distributed, and thus it is difficult to directly compare the Raman spectra of the different samples. Therefore, for each sample the spectrum that showed the largest amount of tetragonal phase was selected (see Fig. 6). Up to 7.6 GPa, no strong transformation of  $\text{ZrO}_2$  can be observed, but only the merging of the two lines at  $305 \text{ cm}^{-1}$  and the appearing band at  $260 \text{ cm}^{-1}$ . The latter belongs to the tetragonal phase and indicates the beginning of the phase change. In the sample irradiated at 11.1 GPa, areas that underwent a pronounced transformation to the tetragonal phase were found. For a pressure of 13.6 GPa, the transformation is slightly stronger than for 11.1 GPa. The originally prominent bands of the monoclinic phase at 180 and  $190 \text{ cm}^{-1}$  vanished almost completely. The degree of transformation is even more advanced than for the irradiation with  $5 \times 10^{12}$  U-ions/ $\text{cm}^2$  at the

UNILAC, where the electronic energy loss was about 40% higher compared to the irradiation at the SIS. The pressure applied during the irradiation obviously plays an important role in the mechanism of the monoclinic-tetragonal transformation since at higher pressures the tetragonal phase reaches a higher fraction. Reference samples showed that neither pressure nor irradiation with  $1.5 \times 10^{11}$  U-ions/cm<sup>-2</sup> alone could induce this degree of transformation, and therefore the effect must be linked to the combination of both.

Several authors tried to explain the mechanism of the monoclinic-tetragonal transformation induced by high-energetic as well as low-energetic heavy ions [28][29][12][15]. Investigation of the development of the tetragonal phase as a function of fluence showed a sigmoidal curve with saturation at about 85% tetragonal ZrO<sub>2</sub> [14][15][12]. This sigmoidal behavior suggests a mechanism for the phase transition which needs two ion impacts [30][8][12]. The first ion is assumed to create defects, mainly oxygen vacancies, that generate an important strain field in the neighborhood in the monoclinic phase of ZrO<sub>2</sub> and might be responsible for lowering the transition temperature [27][12]. These local strain fields are necessary to trigger the phase transformation by the second ion impact.

This might be an explanation why a pressurized sample displays this transformation already at fluences more than one magnitude lower than needed at ambient pressure conditions. A sufficiently high pressure induces a strain that otherwise has to be created by the first ion impact. In this case, the first ion takes over the part of the second ion in triggering the phase transition, and a double impact is no longer necessary. This could also explain why the transformation appears only locally within the sample. At  $1.5 \times 10^{11}$  ions/cm<sup>2</sup>, about 10% of the sample area has been covered by ion hits assuming a track diameter of about 10 nm. It should be noted, that Raman Spectroscopy allows us to detect this displacive phase transition only if the area reaches an extension of several  $\mu\text{m}^2$ .



## 4 Conclusion

This work presents first results of effects in  $\text{ZrO}_2$  irradiated at various pressures with relativistic Pb and U ions. We demonstrated that the phase transition from monoclinic to tetragonal  $\text{ZrO}_2$ , which is known to occur under high-fluence irradiation [14][27][12], begins at fluences more than one magnitude lower if the pressure exceeds 11 GPa. Reference experiments showed that neither pressure nor irradiation alone can provoke such a strong transformation. Obviously the combination of both parameters plays a crucial role in the transformation mechanism. The pressure must exceed a certain value in order to initiate the transformation and further pressure increase enhances this process. The phase transformation is not homogeneous throughout the sample volume. In contrast to irradiation at ambient conditions it appears only locally and the degree of the transformation varies strongly depending on the measured position. This may indicate that under pressure the structural transition does not require a double hit process, because pressure takes over the role of the first ion by inducing a strain field within the sample.

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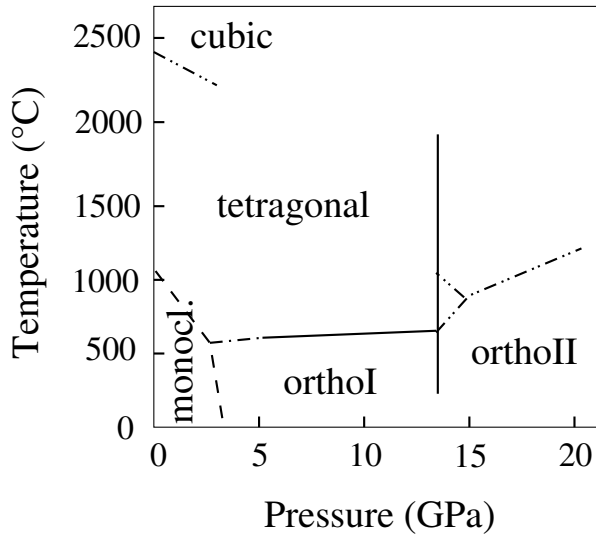


Figure 1: Phase diagram of  $\text{ZrO}_2$  [7]

Sample	Ion	Pressure [GPa]	Fluence [ions/cm <sup>2</sup> ]	$E_i$ [GeV]	$E_f$ [GeV]	$dE/dx$ [keV/nm]
<b>SIS beam</b>						
ZrO <sub>2</sub> 01	<sup>208</sup> Pb	10.9	$2.5 \times 10^{11}$	204	35	30
ZrO <sub>2</sub> R1	<sup>208</sup> Pb	ambient	$2.5 \times 10^{11}$	204	35	30
ZrO <sub>2</sub> 02	<sup>238</sup> U	4.3	$1.5 \times 10^{11}$	228	39	37
ZrO <sub>2</sub> 03	<sup>238</sup> U	7.6	$1.5 \times 10^{11}$	228	39	37
ZrO <sub>2</sub> 04	<sup>238</sup> U	11.0	$1.5 \times 10^{11}$	228	39	37
ZrO <sub>2</sub> 05	<sup>238</sup> U	13.6	$1.5 \times 10^{11}$	228	39	37
ZrO <sub>2</sub> R2	<sup>238</sup> U	ambient	$1.5 \times 10^{11}$	228	39	37
ZrO <sub>2</sub> 06	<sup>238</sup> U	11.2	$1.5 \times 10^{11}$	228	39	37
<b>UNILAC beam</b>						
ZrO <sub>2</sub>	<sup>238</sup> U	ambient	$5 \times 10^{10} - 5 \times 10^{12}$		2.64	53
ZrO <sub>2</sub>	<sup>208</sup> Pb	ambient	$5 \times 10^{10} - 7.5 \times 10^{12}$		2.31	42

Table 1: Parameters of irradiation experiments.  $E_i$  denotes the initial kinetic ion energy and  $E_f$  the ion energy when reaching the sample.  $dE/dx$  is the mean electronic energy loss deposited in the sample. The values were calculated with the SRIM 2006 code [31] taking into account the different in-beam components (detector foils, exit window, air gap, and anvil).

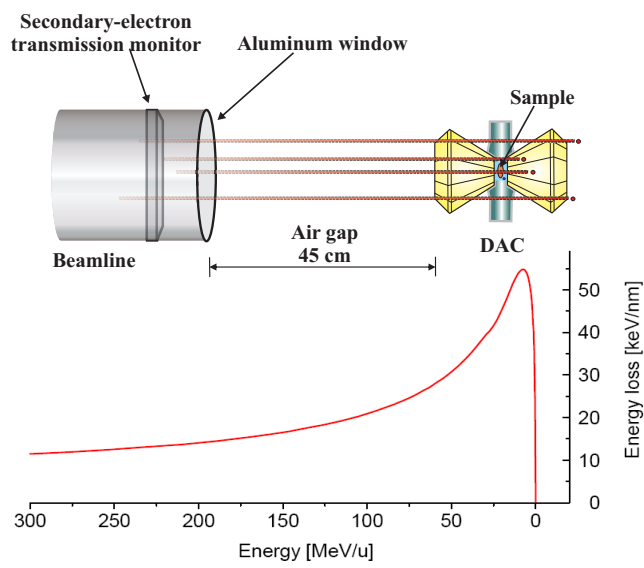


Figure 2: Schematics of sample irradiation at the heavy-ion synchrotron SIS (not to scale) [3]. Before reaching the sample, the beam exits the beamline through an Al-window and travels through 45 cm air and 2.6 mm diamond. The energy, energy loss, and ion range is estimated by calculation with the SRIM06 code [31].

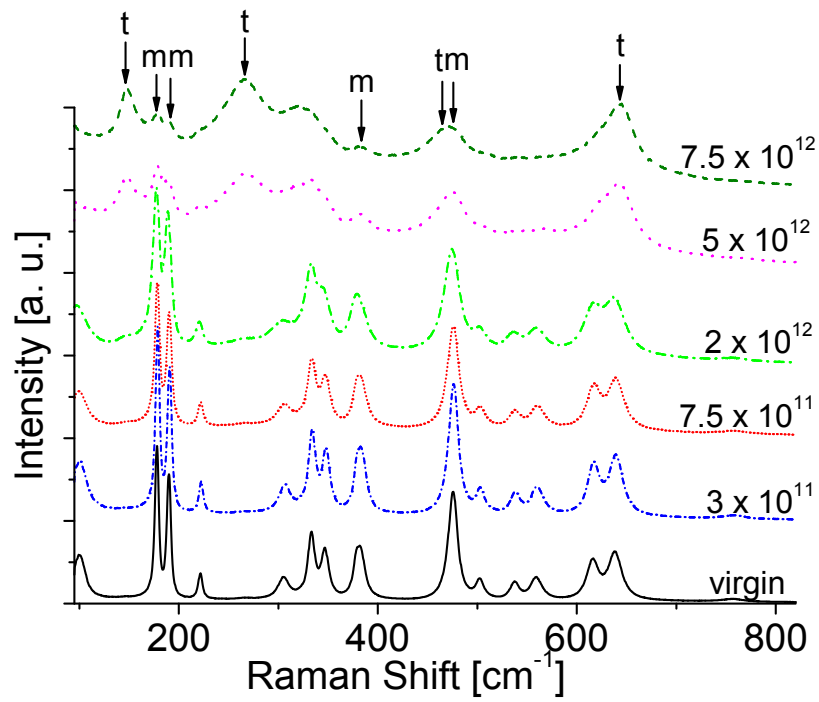


Figure 3: Raman spectra of  $\text{ZrO}_2$  irradiated with Pb-ions (2.3 GeV) of various fluences ions/cm<sup>2</sup>

. Bands labeled as t (m) are ascribed to the tetragonal (monoclinic) phase.

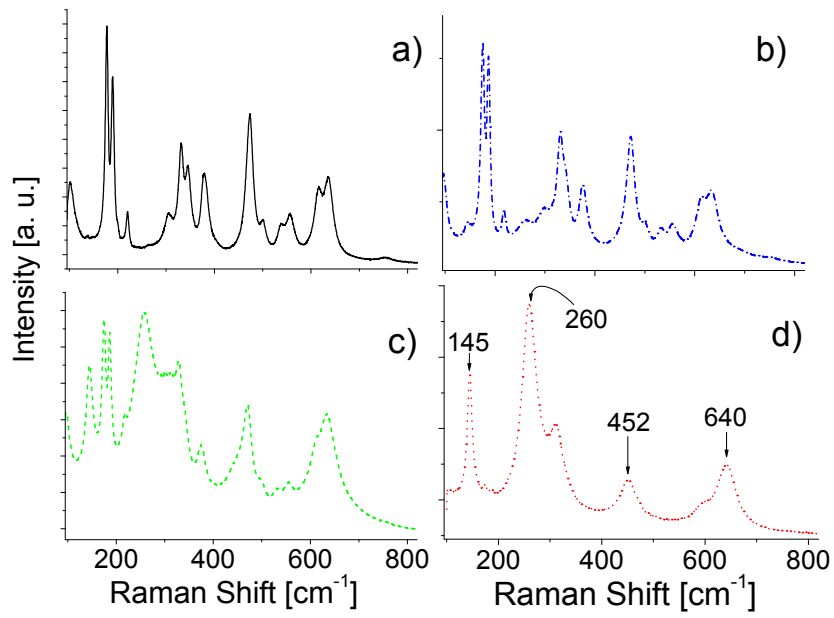


Figure 4: Raman spectra recorded outside the DAC at different positions of sample ZrO<sub>2</sub>-01 (see Table 1) irradiated at 10.9 GPa with  $2.5 \times 10^{11}$  Pb-ions/cm<sup>2</sup>.

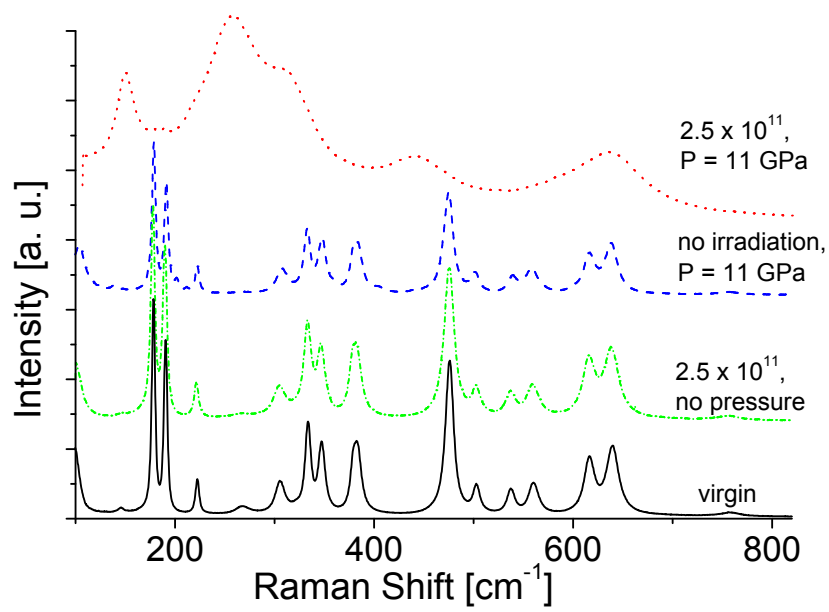


Figure 5: Raman spectrum of sample ZrO<sub>2</sub>-01 (dotted line, irradiated under pressure) compared to reference samples only exposed to either irradiation (dash-dotted) or pressure (dashed) and virgin ZrO<sub>2</sub>.



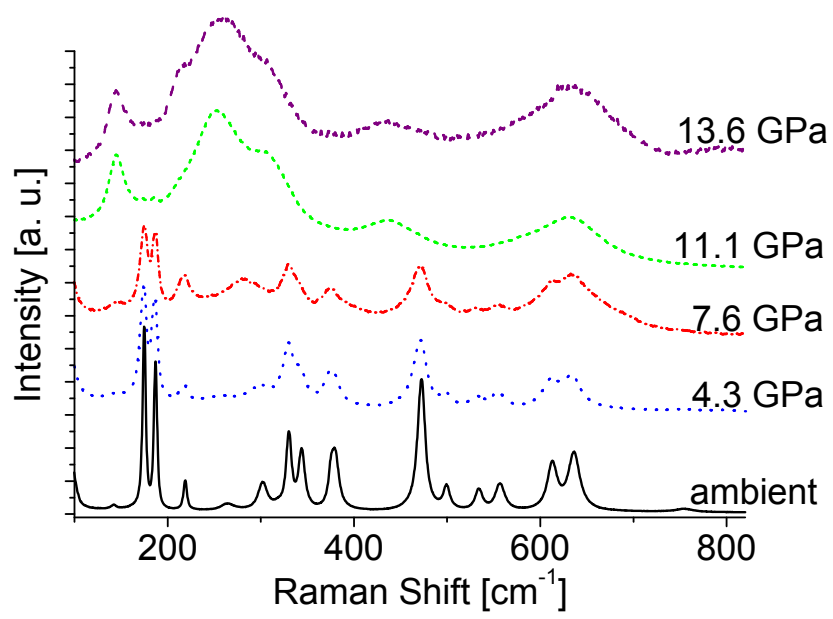


Figure 6: Raman spectra recorded outside the DAC of samples ZrO<sub>2</sub> 02 - 05 and R2 irradiated with  $1.5 \times 10^{11}$  U-ions/cm<sup>2</sup> at various pressures.