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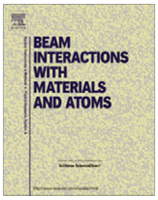

Response behavior of ZrO_2 under swift heavy ion irradiation with and without external pressure

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ABSTRACT

In this study, we demonstrate that the combination of relativistic heavy ions with pressure can influence the phase behavior of ZrO_2 in ways none of those two extreme conditions alone could. The response behavior of ZrO_2 towards ion irradiation under different pressure conditions is investigated. ZrO_2 exposed to energetic particles is known to undergo a crystalline-to-crystalline phase transition from the monoclinic to the tetragonal phase. In agreement with earlier findings, this structural change requires also for heaviest ions, such as Au, Pb, and U, a multiple ion impact. If the irradiation is performed under high pressure, the monoclinic-to-tetragonal transformation occurs at a fluence that is more than one order of magnitude lower suggesting a single impact process. Raman measurements at ambient conditions and X-ray diffraction analysis of the samples irradiated under pressure revealed that the monoclinic-to-tetragonal transformation under pressure is not a direct process but involves a transition into the cubic high-temperature structure, before the tetragonal structure becomes stable under decompression. At even higher pressures, the additional ion irradiation forces ZrO_2 to transform to the higher orthorhombic-II phase that is far away from its stability field.

1. Introduction

On passing through a solid, swift heavy ions slow down and transfer their kinetic energy to the target electrons by ionization and excitation processes. In most solids, predominantly in insulators, the high, localized energy deposition leads to the formation of tracks, cylindrical damage regions (often consisting of amorphized material) a few nm in diameter surrounded by the pristine, undamaged matrix [1,2]. Ion tracks are characterized by severe chemical, physical, and structural modifications. In non-amorphisable crystals, the track region contains numerous lattice defects [3,4] and/or has undergone a transition to a different crystalline phase [5]. Until recently, most irradiations were performed at ambient pressure conditions. Here we describe a relatively new experimental approach by combining ion irradiation with high pressure [6]. Pressure applied during irradiation not only opens the access to a large variety of structural conformations of the starting material but also allows new routes for phase transitions within the *p-T* phase diagram. Additional pressure was shown to enhance or hinder certain radiation induced transformations [7,8]. Conversely, ion irradiation can change the stability field of some materials [6,9]. The exposure of pressurized samples to ion beams also provides insight how pressure-induced phase transitions in minerals may be affected by pre-existing damage and by the microstructure of the starting material. Recent results demonstrated that new structural phases may become accessible [7]. In this study we concentrate on ZrO_2 (zirconia) and its response to ion irradiation and pressure. Zirconia is known for its high fracture toughness, low thermal expansion, high refractoriness, high resistance to wear and corrosion, and especially chemical inertness. Because of these properties, ZrO_2 is one of the most important functional ceramics [10]. It is used, e.g., as inert fuel matrix in nuclear reactors [11–13] or as containment material for radioactive waste [14,15]. Important for our experiments is the existence of several structural polymorphs and the fact that ion irradiation at ambient pressure leads to a structural transition from the monoclinic to the tetragonal phase [16]. Depending on pressure and temperature, zirconia has five known structural conformations: at ambient pressure and temperature conditions, ZrO_2 exists as a white powder in its monoclinic phase (also called baddelyte). At temperatures around 1170 °C, zirconia transforms to its tetragonal high-temperature form accompanied by a density increase of $\sim$4–5% [17]. At 2370 °C, a transformation to the cubic structure occurs, before melting sets in around 2700 °C [14]. Zirconia also exhibits two high pressure phases, but the exact boundaries are not well defined, although numerous groups (e.g., [18–23]) have performed high-pressure experiments.

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Table 1
Irradiation and pressure parameters for all samples irradiated at the UNILAC at ambient pressure and for those irradiated at the SIS under high pressure. The table summarizes the crystalline structures before and after irradiation, as determined at ambient conditions.

Ion	E_{init} (GeV)	dE/dx (keV/nm)	Fluence Φ (ions/cm^2)	Pressure (GPa)	Initial structure	Final structure	Radius (nm)
UNILAC beam							
^{238}U	2.64	53	0.05–1.0 $\times 10^{13}$	Ambient	Mono	Tetragonal for $\Phi \geqslant 5 \times 10^{12}$	5.3
^{208}Pb	2.31	42	0.05–7.5 $\times 10^{12}$	Ambient	Mono	Tetragonal for $\Phi \geqslant 7 \times 10^{12}$	4.4
^{197}Au	2.19	40	0.05–1.8 $\times 10^{13}$	Ambient	Mono	Tetragonal for $\Phi \geqslant 1 \times 10^{13}$	4.0
SIS beam							
^{238}U	7.14	39	1.5×10^{11}	11.0 ± 0.3	Ortho-I	Strong tetragonal regions	
^{238}U	7.14	37	1.5×10^{11}	Ambient	Mono	Mono	
^{238}U	7.14	39	2.0×10^{12}	10.3 ± 0.3	Ortho-I	Cubic (10 GPa), tetragonal (ambient)	
^{238}U	7.14	37	2.0×10^{12}	Ambient	Mono	Mono	
^{238}U	7.14	$\geqslant$39	1.5×10^{12}	23 ± 1.0	Ortho-I	Ortho-II	
^{238}U	7.14	$\geqslant$39	1.5×10^{12}	38 ± 2.0	Ortho-II	Ortho-II	
^{238}U	7.14	$\geqslant$39	1.5×10^{12}	70 ± 4.0	Ortho-II	Ortho-II	

The problem arises from the fact that high-pressure transitions often occur quite sluggishly and are not easily identified. At pressures between 4 and 7 GPa, the transition from the monoclinic to the first high-pressure phase, orthorhombic-I (space group Pbca, polyhedral coordination of seven), takes place [24,19]. This displacive transition is well defined at room temperature and depends on the crystallite size. Even at pressures around 10 GPa and room temperature, the transition is not complete, but residues of the monoclinic phase are detectable. The orthorhombic-I phase is not quenchable to ambient conditions. At elevated temperatures >600 °C, the transition into a second high-pressure phase, orthorhombic-II (space group Pnma, polyhedral coordination of nine), takes place at 12.5 GPa. This transition is quite temperature dependent [18,21,24,25]. At room temperature, it occurs between 25 and $\geqslant$30 GPa [18–20,24,25,21,26–28]. Because the ortho-I-to-ortho-II transition is reconstructive [29], it is not surprising that it becomes increasingly sluggish at ambient temperature and usually an excess pressure of >10 GPa is needed for complete transformation [24]. This additional energy investment results in the increased stability of the orthorhombic-II phase, and is quenchable to ambient pressure [24,25,29]. The ortho-I-to-ortho-II transformation requires a significant reorganization of the cation and anion sublattices, increasing the coordination number of Zr^{4+} from seven to nine, and therefore the transformation kinetics are slowed down to the point of being irreversible at room temperature [21]. At ambient pressure, the radiation response of zirconia has been studied extensively for low-energy ions at room [30–33] and cryogenic [13] temperatures, as well as for swift heavy ions [5,34–39]. All cited experiments showed that for very high ion fluences a structural phase transition from the monoclinic to the high-temperature tetragonal phase occurs. For experiments performed with low-energy ions in the nuclear stopping regime (e.g., Ge, Kr, or Xe-ions of energy around 300 keV), the transformation occurs only in a surface layer of few hundred nm [33] and requires fluences around 10^{18}–10^{19} ions/cm^2 [30]. For swift heavy ions with high electronic stopping (Ni, Ge, Kr, I, and Xe of energies up to about 10 MeV per nucleon (MeV/u)), the monoclinic-to-tetragonal transition requires a critical energy loss of 12 keV/nm [40] and saturates at fluences above 1×10^{13} ions/cm^2 [34], much lower than for beams in the elastic collision regime. Compared to the earlier results, all irradiations presented here were performed with heavy ion species Au, Pb, and U. Moreover, we concentrate on how pressure influences the ion-induced damage process by comparing ZrO_2 irradiated under ambient and various high pressures.

2. Experimental

The irradiations of zirconia samples were performed at two different beamlines of the accelerator facilities at the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany. Experiments at ambient pressure were carried out at the UNILAC (Universal Linear Accelerator) using ^{197}Au, ^{208}Pb, and ^{238}U ions of 11.4 MeV/u, while irradiations of samples pressurized in diamond anvil cells required energies between 150 and 200 MeV/u available at the heavy ion synchrotron SIS. In both cases, the stopping process of the ions is dominated by electronic excitation, i.e., the nuclear energy loss via elastic collisions of projectiles with atoms of the sample can be neglected. All irradiations were performed at room temperature and under normal beam incidence. For the irradiation at ambient pressure, powder samples (purchased from Sigma–Aldrich) were fixed at thin indium foils. During ion exposure, the beam flux and fluence were controlled via a secondary electron transmission monitor (calibrated with a standard Faraday cup) that reduces the initial beam energy to 11.1 MeV/u. The range of all ions in ZrO_2 was ~60 μm [41]. The ion flux was limited to ~ 2–5×10^8 ions/cm^2 to avoid macroscopic sample heating. Fluence series covered values from 1×10^{11} up to 1×10^{13} ions/cm^2. The averaged electronic energy loss $(dE/dx)_e$ within the sample was 40 keV/nm for Au, 42 keV/nm for Pb, and 53 keV/nm for U ions, calculated with the SRIM 2008 code [41]. All irradiation parameters are listed in Table 1.

For high pressure application, we used diamond anvil cells (DAC) consisting of two opposing diamonds with the sample compressed between the culets. Based on the simple principle of $P = F/A$, the pressure P is obtained by exerting a force F on the

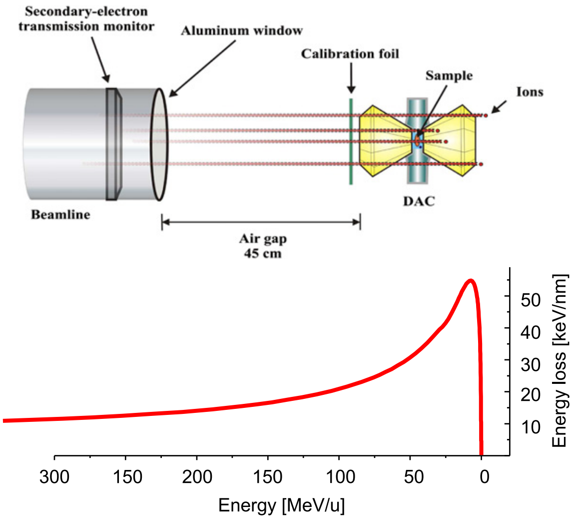

Fig. 1. Schematic of sample irradiation inside a diamond anvil cell at the heavy ion synchrotron SIS (not to scale). Before reaching the sample, the beam exits through an Al window and travels across 45 cm of air and ~2 mm of diamond. The initial ion energy is selected such that the energy loss maximum lies tightly behind the sample.