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Ion tracks and microstructures in barium titanate irradiated with swift heavy ions: A combined experimental and computational study

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Abstract

Tetragonally structured barium titanate ($BaTiO_3$) single crystals were irradiated using 635 MeV $^{238}U^{+}$ ions to fluences of 1×10^7, 5×10^{10} and 1.4×10^{12} ions cm^{-2} at room temperature. Irradiated samples were characterized using ion channeling, X-ray diffraction, helium ion microscopy and transmission electron microscopy. The results show that the ion-entry spot on the surface has an amorphous core of up to ~10 nm in diameter, surrounded by a strained lattice structure. Satellite-like defects around smaller cores are also observed and are attributed to the imperfect epitaxial recrystallization of thermal-spike-induced amorphization. The critical value of the electronic stopping power for creating observable amorphous cores is determined to be ~22 keV nm^{-1}. Molecular dynamics simulations show an amorphous track of ~1.2 nm in radius under thermal energy deposition at 5 keV nm^{-1}; the radius increases to ~4.5 nm at 20 keV nm^{-1}. A linear fit of the core diameter as a function of the square root of the energy deposition rate suggests a reduction in the diameter by an average of ~8.4 nm due to thermal recrystallization if electron–phonon coupling efficiency of 100% is assumed. The simulation also reveals details of the bonding environments and shows different densities of the amorphous zones produced at different energy deposition rates.

Keywords: Swift heavy ion irradiation; Ion track; Molecular dynamics simulation; Barium titanate

1. Introduction

Barium titanate ($BaTiO_3$) is a technologically important ceramic with outstanding ferroelectric, dielectric and optical properties [1–3]. Current applications of the material include fabrication of transducers [4], ceramic capacitors [5], self-regulating electric heating systems [6], self-pumped phase conjugation [7] and thermal cameras [8]. This ceramic material also has potential for applications in semiconducting devices [2] and is being currently explored for possible millimeter-wave applications [9]. It is yet to be determined how impactful the material will be in other fields of importance, including nuclear energy systems and space stations where high nuclear radiation is present. The response of $BaTiO_3$ single crystals to MeV ion irradiation as well as their thermal properties of phase transitions have been previously investigated [10,11]. For 1.0 MeV Au^{2+} ion irradiation at 300 K, complete amorphization occurs at an ion fluence of 1.5×10^{13} Au^{2+} cm^{-2} [11], indicating that the material can be readily amorphized. Several recovery stages have been identified in the post-irradiation thermal annealing process, including a temperature range between 720 and 870 K for epitaxial recrystallization [11]. However, both experimental and computational studies of $BaTiO_3$ under swift heavy ion (SHI) irradiation are still absent to date. The behavior of this material under electronic energy deposition at an

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extremely high rate is currently unknown. It is important to improve understanding of the phase stability of the material driven far from the equilibrium state by SHI irradiation.

It is known that $BaTiO_3$ crystals can exist in five different polymorphic forms with a melting point of 1898 K [12]. The crystalline phases are rhombohedral ($T < 183$ K), orthorhombic (183 K $< T <$ 278 K), tetragonal (278 K $< T <$ 403 K), cubic (403 K $< T <$ 1713 K) [13] and hexagonal (1713 K $< T <$ 1898 K) [14]. As a result of heat dissipation from a thermal spike induced by SHI irradiation [15], the temperature near the region of an ion path will increase. For instance, in silica irradiated with 360 MeV Xe^+ ions at 100 K, thermal spike calculations [16] show that the lattice temperature reaches up to 8400 K from 3×10^{-14} to 4×10^{-13} s at a distance of 1 nm from the ion path and decreases to 2600 K from 6×10^{-14} to 5×10^{-12} s at 4 nm. At 0.1 ns, the temperature still remains above 1000 K within 4 nm from the ion path. The rate of the temperature decrease becomes smaller as time increases. Similar studies for SHI irradiated $BaTiO_3$ do not exist, but it is possible that, in a transient process of a thermal spike induced by SHI irradiation, the temperature within a radius can be maintained between 1713 and 403 K for up to nanoseconds or longer so that phase transition to cubic structure could occur. This time length is generally required for lattice relaxation and phase transition [17]. Assuming that the heat dissipation is uniform along the direction perpendicular to the ion trajectory, a ring of cubic phase would be expected to form during the transient process. This ring should be surrounded by tetragonal phase where the temperature is maintained between room temperature (~296 K) and 403 K all the time. Hexagonal phase is not expected in this study due to extremely short duration above 1713 K; similarly, orthorhombic or rhombohedral phase should not emerge because the material temperature was never below room temperature. However, it still remains to be investigated whether the expected cubic rings can be quenched fast enough to be observable in ambient conditions.

Latent ion tracks have been observed in many SHI-irradiated ceramic materials. Tracks form upon fast quenching of a melting state induced by a high-density energy deposition along the ion path. There is a critical rate dE/dx of the electronic energy deposition for the track formation, which is material-composition-dependent. Two critical thresholds for CaF_2 have been recently determined for formation of core–shell structured tracks from quenching of boiling and molten phases, respectively [18]. Depending on the strength of chemical bonds, ion tracks can be in the amorphous state or a crystalline phase with defects, where thermodynamic and kinetic processes also play a key role. Previous studies suggest that materials with stronger ionic bonding are less likely to form amorphous tracks under SHI irradiation [18]. The differences in amorphization tendency between titanate and zirconate pyrochlores has been related to the difference in their iconicity [19]. In a recent study [17], the experimental results from SHI-irradiated ceramic compositions of $Gd_2O_3(TiO_2)_x$ ($x = 1$, 2) and $Gd_2Zr_{2-x}Ti_xO_7$ ($x = 0$, 1) show that the ion tracks contain an amorphous core with a crystalline shell that has a hexagonal phase in Gd_2TiO_5 and a defect-fluorite structure in gadolinium titanate pyrochlore ($Gd_2Ti_2O_7$); in the case of gadolinium zirconate pyrochlore ($Gd_2Zr_2O_7$), the track core has a defect-fluorite structure as also reproduced by molecular dynamics (MD) simulations. When a high pressure is applied during SHI irradiation of $Gd_2Zr_2O_7$, a body-centered-cubic lattice is obtained even after pressure release and quenching in ambient conditions for an extended period of time [20]. Studies of latent tracks, associated defect structures and phase transitions induced by SHI irradiation in various materials including amorphous silica [21,22], metals [23,24] and various types of ceramics, such as $CaZrO_3$ perovskite [25], pyrochlores [17,26,27], A_2TiO_5 (A = La, Nd, Sm, and Gd) compositions [28] and zirconia [29,30] have shed light on the dynamical processes that govern track formation. However, there is a need to understand the thermodynamic driving forces and kinetics of phase transformations caused by swift heavy ion irradiation. In an effort to illuminate fundamental atomic-level processes that result in ion tracks and their surrounding microstructures in ceramics, the present work combines experiment and computer simulation to study single-crystal $BaTiO_3$ irradiated with 635 MeV $^{238}U^+$ ions.

2. Experimental procedure and simulation approach

2.1. Experimental procedure

A (100)-oriented, tetragonally structured single crystal of $BaTiO_3$ with an area of 10×10 mm^2 was cut into four pieces of equal area (5×5 mm^2) for this study. One of the samples was reserved for a comparison study; the other three were irradiated with 635 MeV $^{238}U^+$ ions at the GANIL facility in Caen, France, to fluences of 1×10^7, 5×10^{10} and 1.4×10^{12} ions cm^{-2}, respectively, at room temperature in vacuum (~10^{-6} mBar). While the two lower-dose samples maintained their integrity, the one with the highest dose broke into a few pieces (see discussion below).

Subsequent characterizations of the unirradiated and irradiated samples have been carried out within the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory using Rutherford backscattering spectrometry under ion-channeling conditions (RBS/C), X-ray diffraction (XRD) and helium ion microscopy (HIM). Using a 3.0 MV electrostatic tandem ion accelerator, room-temperature RBS/C along the ⟨100⟩-axial direction with 2.0 MeV He^+ ions at a scattering angle of 150° was performed to assess the overall damage level of the samples within an area of the probe size (~1×1 mm^2). Both a Philips X'pert Multi-Purpose Diffractometer (MPD) and a Materials Research Diffractometer (MRD), having a fixed Cu anode operating at 45 kV and 40 mA, were used. The MRD is a high-resolution diffractometer with a