

Ion Irradiation-induced Amorphization in Vanadate-Phosphate Apatites

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The apatite-type structure, $A^I_4A^{II}_6(BO_4)_6(OH, F, Cl)_2$ ($A^I, A^{II} = Ca, Na, \text{rare earths, fission products and/or actinides}$; $B = Si, P, V, \text{ or Cr}$), offers unique structural advantages as an advanced waste form for complex waste streams because of its structural and chemical flexibility, as well as its high chemical durability. A wide range of high concentration waste components (e.g., tri- and tetra-valent actinides, fission products, and processing contaminants, etc.) can be incorporated into the apatite structure-type by coupled substitutions at the cation, as well as anion sites. Importantly, iodine can be incorporated into the structural channels of a lead vanadate-phosphate apatite, $Pb_{10}(VO_4)_{4.8}(PO_4)_{1.2}I_2$.

Radiation effects in apatite compounds, specifically for natural minerals and fluorapatite, have been extensively studied for different types of irradiation sources. Generally, apatite ceramics display an excellent ability to anneal defects, even at low temperatures ($\sim 60^\circ\text{C}$) such that durability is not compromised even under high radiation fluxes experienced during storage or disposal for waste form applications. Ion beam irradiations were performed to investigate radiation damage processes occurred in synthetic apatites including fully phosphate fluorapatite, mono-silicated fluorapatite, synthetic britholite and fully silicated apatite. Amorphization occurred in these synthetic apatites upon heavy ion irradiations resulting from ballistic interactions; while ionization is responsible for amorphization in apatites upon swift heavy ion irradiation above a critical electronic energy loss, below which ionization will lead to enhanced dynamics for defect annealing.

In this study, we performed ion beam irradiation using 1 MeV Kr^{2+} on the series of vanadate-phosphate fluorapatite with the goal in understanding the effects of V/P ratio on the damage production and defect annealing processes. The ion irradiations were conducted using IVEM-Tandem facilities at Argonne National Laboratory at room temperature combining with in-situ TEM observations. The critical amorphization fluences were determined for different apatite compositions from selected area electron diffraction patterns and converted into the universal dose of dpa (displacements per atoms) by SRIM-2008 calculations. The displacement energies employed for SRIM calculations are 28 eV for oxygen and 25 eV for other elements. Figure 1 shows a sequence of SAED patterns of fully phosphate fluorapatite upon 1 MeV Kr^{2+} at room temperature, and a crystalline-to-amorphous structural transformation was observed at a dose of 0.73 dpa, suggesting that radiation damage from ballistic interaction caused the amorphization of apatite structure. The critical amorphization dose for fully phosphate fluorapatite (0.73 dpa) is significantly greater than that the literature data (0.3 dpa and 0.45 dpa for 1.5 MeV Kr^+ and 320 keV Pb^+ , respectively).

Similar to fully phosphate apatite, ion irradiation-induced amorphization also occurred in vanadate apatite without phosphate doping at a much lower damage level. The in-situ high resolution TEM (HRTEM) images (Figure 2) show a gradual disruption of the crystalline lattice of $Ca_{10}(VO_4)_6F_2$ upon 1 MeV Kr^{2+} irradiation at room temperature with increasing fluences. The SAED patterns (inset in Figure 2) also confirmed the amorphization processes. In-situ HRTEM image at a fluence of

6.25×10^{13} ions/cm² shows the formation of amorphous domains upon irradiation at a relatively low fluence, suggesting that direct impact process may be responsible for the amorphization occurred in vanadate, consistent with that observed for fully phosphate fluorapatite upon 320 keV Pb⁺ irradiation. In addition to the amorphous domains resulting from direct impact of heavy ions, some damaged zones with discolored contrast and sub-grain boundaries also formed along certain crystallographic directions, suggesting complex processes of radiation damage in apatite compounds. By substituting phosphate at vanadium site, the critical amorphization dose increases exponentially. The increasing critical amorphization dose and thus enhanced amorphization resistance for phosphate apatite can be attributed to easy rearrangement of PO₄ tetrahedral group upon irradiation for better efficiency of defect annealing. Furthermore, the greater amorphization resistance is consistent with the trend of increasing ratio of electronic to nuclear stopping power (ENSP) based on SRIM calculations, in which the ionization process resulting from electronic energy loss may lead to enhanced annealing of defects upon radiation damage.

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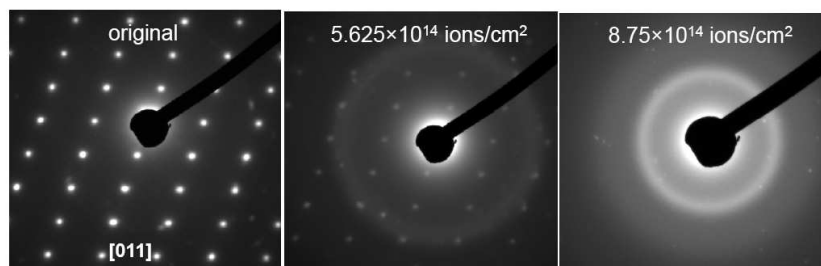


FIG. 1. A sequence of selected area electron diffraction patterns of Ca₁₀(PO₄)₂F₆ upon 1 MeV Kr²⁺ irradiation at room temperature at different fluences. The disappearance of diffraction maxim at high fluence shows radiation-induced amorphization occur in fully phosphate fluorapatite, and the critical dose at room temperature is 0.73 dpa.

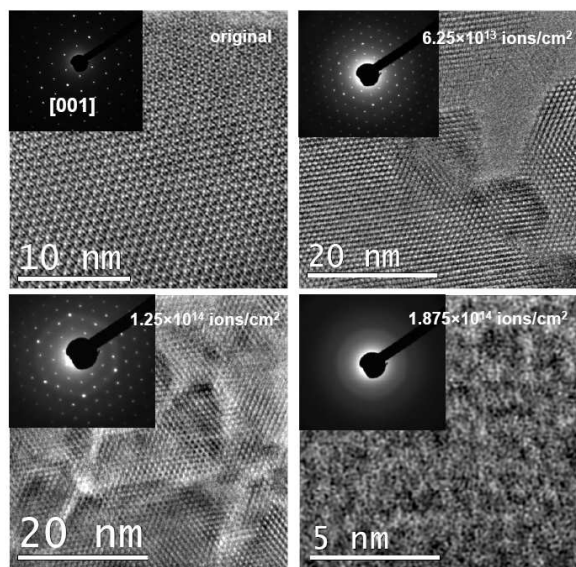


FIG. 2. In-situ high resolution TEM images and corresponding selected area electron diffraction pattern of Ca₁₀(VO₄)₆F₂ upon 1 MeV Kr²⁺ irradiation at room temperature.

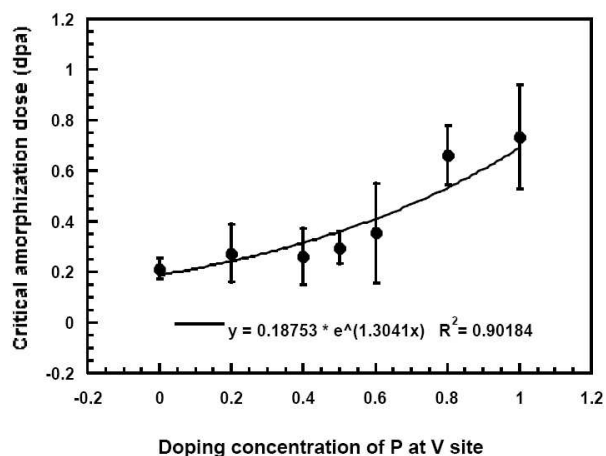


FIG. 3. Critical amorphization dose (dpa) as a function of doping concentration of phosphate at vanadium site in vanadate phosphate fluorapatite.