Probing the effect of radiation damage on the structure of rare-earth phosphates

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ABSTRACT

Synthetic analogues of naturally occurring monazite (REPO$_4$; RE = La to Gd) and xenotime (RE′PO$_4$; RE′ = Tb to Lu and Y) minerals have been identified as potential wasteforms for nuclear waste. High energy ion-implantation of crystalline materials simulates radiation-induced structural damage and allows for the radiation resistance of a crystal structure to be probed. The structural stability of Au$^-$ ion-implanted La$_{1-x}$Yb$_x$PO$_4$ materials was investigated using micro-X-ray diffraction (μ-XRD) and glancing angle X-ray absorption near-edge spectroscopy (GA-XANES) in this study. The long- and short-range order of La$_{1-x}$Yb$_x$PO$_4$ (x = 0, 0.3, 0.7, 1.0) is affected by ion-implantation and, thus, the materials are prone to structural damage. The structures of some members of the La$_{1-x}$Yb$_x$PO$_4$ series (x = 0.7 and 1.0) were observed to partially recover after being implanted with Au$^-$ ions to a high dose. The structures of all members of the La$_{1-x}$Yb$_x$PO$_4$ series were observed to recover from damage resulting from ion-implantation after annealing the materials at temperatures ≥300 °C.

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1. Introduction

Single- and multi-phase crystalline ceramics that are resistant to radiation damage have been proposed as candidate materials for encapsulating radioactive waste [1–4]. Monazite and xenotime are naturally occurring rare-earth phosphate minerals that are being considered as host-matrices for nuclear waste because of the ability of these structures to contain actinide elements [5–7]. These mineral phases have been observed as solid solutions with one another in igneous and metamorphic rocks [8]. Both the monazite- and xenotime-type rare-earth phosphates possess the same general formula REPO$_4$, where RE represents the rare-earth element. The rare-earth site in monazite and xenotime are occupied by lighter (La to Gd) or heavier rare-earths (Lu to Yb and Y), respectively [9]. Materials adopting the monazite-type structure crystallize in a monoclinic (space group − $P2_1/n$) unit cell while materials adopting the xenotime-type structure (YPO$_4$) crystallize in a tetragonal (space group − $I4_1/amd$) unit cell (Fig. 1) [9–13]. In monazite (e.g., CePO$_4$), the RE^{3+} ion is bonded to nine oxygen atoms (REO$_9$) in a non-symmetrical fashion (point group − C$_s$) whereas in xenotime (e.g., YPO$_4$), the RE^{3+} ion is coordinated to eight oxygen

atoms (REO$_8$) in a symmetrical fashion (point group − D$_{2d}$) [11,13]. A more detailed description of the monazite and xenotime crystal structures can be found elsewhere [9–13].

An actinide element incorporated in a crystalline ceramic can undergo a radioactive decay process during which it may (depending upon the decay process) transform into a new radionuclide by releasing a high-energy α-particle [14]. Because of this decay, the crystalline host matrix could experience structural damage from the recoil energy associated with the daughter product radionuclide and/or from the highly energetic α-particle [14]. Therefore, an issue surrounding actinide containing crystalline ceramics is the tendency of these materials to undergo a radiation-induced crystalline to amorphous transition in a process called metamiction [4,14,15]. This process can have an adverse effect on the chemical durability of the wasteform (i.e., an increase in the leach rate of the sequestered elements) [5,16]. This transition can also be accompanied by a swelling of the wasteform [4,5,14–19]. Naturally occurring mineral samples of monazite and xenotime are known to contain significant amounts of UO$_2$ and ThO$_2$ [6,20]. Despite the presence of radioactive U and Th, the mineral monazite, in particular, has been observed to maintain its structural integrity over a geological timescale and it is because of this resistance to radiation-induced structural damage that monazite-type ceramics have been proposed as a solid-state repository for actinide elements [1,21,22]. On the other hand, the structural stability of the
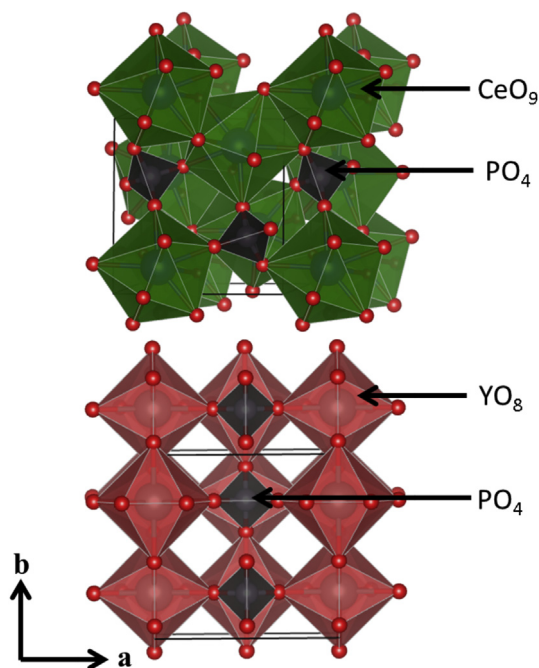
Fig. 1. The crystal structures of (a) $CePO_4$ (Monazite $- P2_1/n$) and (b) YPO_4 (Xenotime $- I4_1/amd$) are shown with the c-axis directed into the page [33]. The crystal structures were generated using the VESTA program [36].

xenotime structure is not well-documented in the literature with the exception of a few studies [6,16,23].

Numerous investigations on the structural stability of natural as well as synthetic monazite samples are reported in the literature [6,24–29]. The structural stability of synthetic monazite samples have been studied either by doping monazite ceramics with actinides (internal irradiation) or by simulating the long-term actinide storage by implantation of the material using high-energy ion beams (external irradiation) [6,24–28]. Since many actinides have a very long half-life, the structural stability of a crystalline wasteform is most often determined by ion-implantation [27]. Heavy ions (such as Au^-, Kr^+, and Ar^+) are generally used to simulate the effects of the daughter product on the crystal structure of a proposed wasteform [6,21,26–28,30,31]. In an early study on the radiation resistance of the monazite structure, Karioris et al. showed the monazite structure to be unstable to heavy ion-implantation; however, they also showed that the damaged monazite structure could be converted back to its original crystalline state after annealing the irradiated material to ~296 °C for 20 h [28]. In another study, Meldrum et al. experimentally determined the critical amorphization temperature (T_c; i.e., the temperature above which the material does not undergo metamiction) of a variety of ion-implanted ternary monazite- and xenotime-type orthophosphates and found the monazite structure to have a lower T_c than the xenotime structure [6]. This observation could suggest that the monazite structure is more resistant to radiation damage than the xenotime structure [6]. In a more recent study, Deschanels et al. performed thermal annealing experiments on Au^- ion-implanted monazite ceramics and studied them using transmission electron microscopy (TEM) [27]. It was shown in this study that complete recrystallization of metamict monazite occurred after annealing the material to 300 °C for 1 h [27]. In addition to observing annealing-induced recrystallization, Deschanels et al. also observed the recrystallization of

amorphous regions in damaged monazite samples under the influence of an electron beam [27]. A theoretical study of the radiation resistance of xenotime (YPO_4) by Urusov et al. shed light on the ability of recoil atoms to bring about a cascade of atomic displacements in this structure [23]. Immediately after the creation of a cascade of atomic displacements, some of the displaced atoms returned to their original crystallographic positions which led to the partial recovery of the xenotime structure [23].

The design of new crystalline wasteforms that are resistant to radiation damage requires a detailed understanding of the electronic structure of a material before and after exposure to radiation. In this context, the electronic structure can be studied using X-ray absorption near-edge spectroscopy (XANES) as it provides information on the local coordination environment, oxidation state, and bonding environment of the absorbing atom [32]. In a previous study, the authors of the present study investigated the electronic structure of three series of monazite–xenotime solid solutions ($La_{1-x}Yb_xPO_4$, $La_{1-x}Y_xPO_4$, and $Sm_{1-x}Ho_xPO_4$) using XANES [33]. It was shown in this study that the P K-edge XANES spectra provide a spectroscopic fingerprint for the monazite and xenotime structures because of the distinct change in spectral lineshape and absorption energy observed between the two structures [33].

The effect of Au^- ion-implantation on the structure of $La_{1-x}Yb_xPO_4$ is discussed in the current study. The La and Yb end-members crystallize in either the monoclinic monazite (x = 0) or tetragonal xenotime (x = 1) structure, respectively. At all other values of 'x', a mixture of both monazite and xenotime phases exist, which allows for an investigation of co-mineralized samples [33]. The Au^- ions used in the study were implanted in the near-surface region of these materials which required the use of surface-sensitive glancing angle XANES (GA-XANES) and micro X-ray diffraction (μ-XRD) to investigate the effect of ion-implantation on the local and long range structure of these materials [34]. The extent of structural damage in $La_{1-x}Yb_xPO_4$ was studied as a function of depth by varying the X-ray angle of incidence during the GA-XANES experiments. This study has allowed for a detailed comparison of the response of the monazite and xenotime structure to ion-implantation. Although GA-XANES has been utilized in determining the structural stability of metal oxides (zirconolites and pyrochlores), no studies exist in the literature on the use of this technique to the investigation of the structural stability of rare-earth phosphates [31,35].

2. Experimental section

2.1. Synthesis and powder XRD

Rare-earth phosphates having the composition $La_{1-x}Yb_xPO_4$ (x = 0.0, 0.3, 0.7, 1.0) were synthesized by conventional solid state methods. Stoichiometric amounts of La_2O_3 (Alfa Aesar; 99.99%), Yb_2O_3 (Alfa Aesar; 99.99%), and $NH_4H_2PO_4$ (Alfa Aesar; 99.995%) were ground and mixed using a mortar and pestle before placing the mixture in an alumina crucible. The crucible containing the mixture was initially heated to 900 °C in air for 1 day to promote the decomposition of $NH_4H_2PO_4$ followed by quench cooling in air. The resulting mixture was ground, pressed into a pellet at a pressure of 6 MPa, and fired at 1100–1200 °C in air for 9 days before being quench cooled in air. The synthesis of $La_{1-x}Yb_xPO_4$ materials was carried out at 1100 °C for the x = 0 material and 1200 °C for all other materials (x = 0.3, 0.7, 1.0). All samples were ground and pelleted every 3 days of heating to ensure the homogeneity of the samples. The hardness of the materials was improved by pressing the materials into pellets at 8 MPa followed by annealing at 1100–1200 °C in air for 3–4 days prior to Au^- ion implantation. The phase purity of the synthesized materials was