2.7 MeV Ar^{11+} ion irradiation induced structural evolution in Lu$_2$(Ti$_{2-x}$Lu$_x$)O$_{7-x/2}$ pyrochlores

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ABSTRACT

This paper aims to study the radiation effects of nonstoichiometric pyrochlore series Lu$_2$(Ti$_{2-x}$Lu$_x$)O$_{7-x/2}$ ($x = 0$–0.667). Polycrystalline Lu$_2$(Ti$_{2-x}$Lu$_x$)O$_{7-x/2}$ samples were irradiated with 2.7 MeV Ar^{11+} ions up to a fluence of 8×10^{14} ions/cm^2. The irradiated samples were characterized using grazing incidence X-ray diffraction technique. The results reveal that Lu$_2$(Ti$_{2-x}$Lu$_x$)O$_{7-x/2}$ samples undergo significant amorphization and lattice swelling upon irradiation. Specifically, the amorphization process is predominantly driven by ballistic nuclear energy deposition of Ar^{11+} ions at this energy regime, which can be well described by a direct-impact/defect-stimulated model. Both the amorphization fraction and the relative variation of lattice parameter decrease with increasing x, showing a strong dependence on the chemical composition. The results are then discussed in the framework of the structural disorder and recovery ability from damage, applying an atomic layer model.

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1. Introduction

Pyrochlores with the general chemical formula of A$_2$B$_2$O$_7$ have been thoroughly investigated during the last decades, due to the large array of structural and physical properties related to their chemical compositions [1,2]. Ordered pyrochlores belong to the $Fd\bar{3}m$ space group which is a superstructure of the ideal fluorite structure ($Fm\bar{3}m$ space group) with one-eighth of the anions removed and two types of cation at the A- and B- sites [1,2]. The stability of the pyrochlore structure is governed by the ratio of the ionic radii of A and B cations (r_A/r_B) which extends from 1.46 for Gd$_2$Zr$_2$O$_7$ to 1.78 for Sm$_2$Ti$_2$O$_7$. Due to the outstanding performance in incorporating radioactive actinides (e.g. U, Np, Th, Pu, Am and Cm) generated through the reprocessing of spent fuel, pyrochlores are now considered as potential immobilization matrices for the high level nuclear wastes [3–6]. Understanding the behavior of complex oxides submitted to radiation is crucial to predict their radiation tolerance, to establish criteria controlling their structural stability and to identify relevant factors for the occurrence of phase transformations [6–8]. Numerous efforts have been devoted to the investigation of radiation effect of pyrochlores by employing ion beam irradiation from particle accelerators [4,6,8–22]. The behavior of materials under ion irradiation is closely correlated with the energy deposition type of ions and the composition of materials. For the low energy regime (i.e., below ~10 keV/u), ballistic process are predominant and directly linked to the nuclear stopping power (S_n) [23]. The elastic collisions between the projectile and the target nuclei lead to the creation of damage cascades. While for the high energy regime (i.e., above 1 MeV/u), the high electronic energy deposition (S_e) of a swift ion induces the formation of an electrostatically unstable cylinder of ionized atoms and the emission of electrons. Latent tracks are generally produced according to the thermal spike model [24].

Although extensive irradiation studies with various ion species and energies have been completed on a variety of A$_2$B$_2$O$_7$ compositions, most of these studies were focused on stoichiometric pyrochlores (A$_2$Ti$_2$O$_7$ and A$_2$Zr$_2$O$_7$) [4,10,16,17,19,25]. According to the temperature-composition (T–C) phase diagram, some pyrochlore phase covers a very broad range of composition in the A$_2$O$_3$–TiO$_2$ binary systems [26,27]. Characteristically, the pyrochlore phases in these systems are nonstoichiometric, on the one hand, with partial A^{3+} substitution for Ti^{4+} and, on the other hand, with partial Ti^{4+} substitution for A^{3+}, which eventually increases the disordering extent of the structure [27,28]. Previous studies have confirmed that A$_2$(Ti$_{2-x}$A$_x$)O$_{7-x/2}$ (A = Gd−Lu, $x = 0$−0.667) can adopt the pyrochlore structure and that the ionic conductivity,

thermal conductivity, magnetic properties and radiation behavior of such solid solutions are effectively tailored by the chemical composition [28–32]. Up to now, the behavior of these non-stoichiometric pyrochlore oxides under radiation conditions is still not fully understood. This paper presents a detailed investigation of Ar^{11+} ion irradiation induced structural evolution in the non-stoichiometric $Lu_2(Ti_{2-x}Lu_x)O_{7-x/2}$ series where $x = 0–0.667$. The $x = 0$ compound possesses the ideal pyrochlore phase stoichiometry, while $x > 0$ compounds are nonstoichiometric Lu-excess pyrochlore compositions. We will refer to these compounds generically as LTO in this text.

2. Experimental

Polycrystalline LTO samples were synthesized from Lu_2O_3 and TiO_2 by conventional ceramic processing procedures. Lu_2O_3 (99.99% purity) and TiO_2 (99.99% purity) oxides with different molar ratios were intimately mixed and ground using a ball-mill and subsequently pressed into pellets at a pressure of ~15 MPa. The pellets were first sintered at 1200 °C for 24 h. In order to increase the homogeneity and density of samples, the procedures (grinding, milling and pressing) were repeated with a second sintering in air at 1450 °C for 48 h. The resulted pellets were finally polished to a mirror finish using the W0.25 Diamond suspension. Samples of five compositions were synthesized, corresponding to $x = 0$, 0.162, 0.286, 0.424 and 0.667. The "x" can be regarded as a compositional parameter which indicates the additional Lu-content in LTO or the deviation of samples from the ideal $Lu_2Ti_2O_7$ stoichiometry. The pristine samples were examined using X-ray diffraction and determined to possess the pyrochlore structure for $x = 0–0.424$ compositions and fluorite structure for $x = 0.667$ composition.

Ion irradiations were carried out at a 320 kV platform for multi-discipline research with highly charged ions at the Institute of Modern Physics, CAS. The 2.7 MeV Ar^{11+} ions were implanted at normal incidence relative to the sample surface, with the fluence ranging from 2×10^{14} to 8×10^{14} ions/cm^2, at room temperature. To estimate ion range and displacement damage, the Ar^{11+} ion transportation in LTO has been simulated using the Monte Carlo SRIM 2008 code [33]. Calculations indicate that the Ar^{11+} ion range in $Lu_2Ti_2O_7$ is ~1.1 μm. We arbitrarily assume 40 eV displacement energies for all elements in these calculations. Note that, due to the same constituent atoms and similar densities, the estimated results for all compositions show little discrepancy which can be neglected.

Irradiated samples were characterized by grazing incidence X-ray diffraction (GIXRD) technique. GIXRD measurements were performed using a Rigaku D/Max-2400 X-ray Diffractometer configured in θ−2θ geometry. The X-ray incidence angle for measurements was chosen to be γ = 1°, so that the estimated X-ray penetration depth is significantly shallower than the projected range of the displacement damage peak [34]. The scan range is $10°−70°$ with a step size of 0.02° and a dwell time of 1 s.

3. Results and discussion

3.1. Structure of the pristine samples

Fig. 1 shows the XRD patterns obtained from the pristine LTO samples. The intensity of each pattern was normalized to the most intense diffraction maximum at 2θ ~31°. It is obvious that each composition possesses single phase (pyrochlore or fluorite, as labeled by P or F). Composition induced structural modifications are evident from two aspects in the XRD patterns: minor shift and variations in the relative intensity of diffraction peaks. All the diffraction peaks shift to lower 2θ with increasing x (as shown in
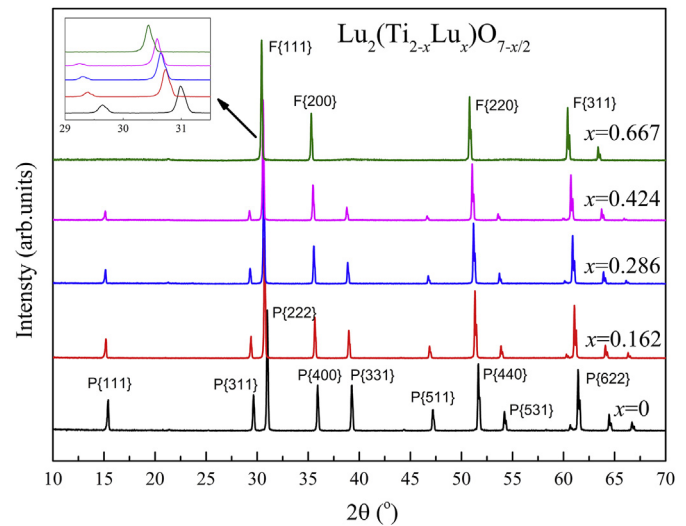

Fig. 1. XRD patterns of pristine LTO samples. "P" represents the pyrochlore structure and "F" represents the fluorite structure. The inset presents an enlarged view of the 2θ = 27.5−32.5° region.

the insets), indicating that the lattice parameter of LTO increases. It is reasonable since the radius of Lu ion is much larger than that of Ti ion. Additional Lu substituting for Ti thus causes local lattice distortion and eventually increases the lattice parameter of LTO. Another aspect, the odd indexed peaks (e.g. {1 1 1}, {3 1 1} and {3 3 1}) are correlated to the disordering extent of LTO samples. Actually diffraction peaks observed are divided into two series. The first series of peaks with even indices are the reflections contributed by both the fluorite sublattice and the pyrochlore superlattice, while those with odd indices are reflections only from the pyrochlore superlattice. Therefore, the intensity decrease of the odd peaks in XRD patterns reveals that the disordering extent of LTO is enhanced with increasing x. All the superlattice diffraction peaks vanish at $x = 0.667$, indicating a disordered fluorite-like structure. These results are in good agreement with the previous studies [28,29,31].

3.2. Radiation damage of the irradiated samples

Fig. 2 displays the normalized GIXRD patterns recorded on the irradiated LTO samples (note: here we present the results of selected compositions in order to avoid the tedious stack of similar patterns). Fig. 2(a–c) show the GIXRD patterns of compounds with $x = 0$, 0.286 and 0.667 over the whole range of irradiation fluence respectively. At the low irradiation fluences of 2×10^{14} and 4×10^{14} ions/cm^2, for compounds with pyrochlore structure ($x = 0$ and 0.286), it is clear that the superlattice diffraction peaks (marked on the graph) diminish with the increasing ion fluence, indicating that Ar^{11+} irradiation induces a transition from an ordered pyrochlore structure to a disordered fluorite structure (O−D) in both compounds. Moreover, as the ion fluence increases to 6×10^{14} ions/cm^2, strong diffuse scattering occurs at the basis of P{2 2 2} peak for $Lu_2Ti_2O_7$ ($x = 0$) composition (as marked with the arrow). This diffuse scattering arises from the formation of an amorphous phase. While for the intermediate composition of $x = 0.286$, no significant diffuse scattering is detected at this fluence, and until the Ar^{11+} ion fluence increases to the maximum 8×10^{14} ions/cm^2, the diffuse scattering becomes obvious, indicating that much more Ar^{11+} ions are required to amorphize $LTO_{x = 0.286}$, as compared with the case of $Lu_2Ti_2O_7$. However, the end member Lu_2TiO_5 ($x = 0.667$) maintains its original fluorite-like structure over the entire range of irradiation fluence, since no significant changes are found in the