



Ion-irradiation-induced structural transitions in orthorhombic Ln_2TiO_5

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Abstract

The response of a material to a high radiation field is important when selecting materials for nuclear applications, such as structural materials, nuclear waste forms and inert matrix fuels. In the present study, the radiation response of orthorhombic, rare-earth titanates, Ln_2TiO_5 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}$ and Y), was investigated by 1 MeV Kr^{2+} ion bombardment at temperatures ranging from 50 to 1073 K. In situ transmission electron microscopy revealed that the radiation tolerance and irradiation-induced structural transitions vary largely with composition. Y_2TiO_5 exhibits the lowest critical amorphization temperature ($T_c = 623$ K), above which crystals cannot be amorphized, which is consistent with its use in the form of nanoclusters in radiation-resistant oxide-dispersion-strengthened steels. The disordered fluorite structure type of Ln_2TiO_5 , with smaller Ln cations, formed as an intermediate phase prior to becoming fully amorphous. The fluorite structure type of Ln_2TiO_5 , containing more vacancies as compared with that of $\text{Ln}_2\text{Ti}_2\text{O}_7$, may exhibit enhanced ionic conductivity, which highlights an effective way of using ion beams to modify the properties of materials.

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1. Introduction

The radiation response of a material determines its physical, chemical and electronic properties, and is an important consideration for materials that are used in high-radiation environments, such as nuclear fuels and nuclear waste forms [1–6]. The change in properties, as a result of irradiation, is due to the formation of interstitial and or vacancy defects, defect clustering, order–disorder transformations and amorphization that can cause swelling, phase decomposition or the formation of new crystalline phases [4,5]. The rate of damage accumulation and annealing is sensitive to the temperature of the irradiation and the subsequent thermal history. The structure and composition of a material provide a critical means of controlling the radiation response. Recently, extensive research

efforts focused on the radiation response within $\text{A}_2\text{O}_3\text{–BO}_2$ binary compounds ($\text{A} = \text{lanthanides}, \text{Y}$ and Sc ; $\text{B} = \text{Ti}, \text{Zr}, \text{Sn}$ and Hf) in order to find radiation-resistant materials (i.e. those that retain their crystalline structure by order–disorder transition instead of radiation-induced amorphization). These compounds, including pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$) [1,7–14] and δ -phase ($\text{A}_4\text{B}_3\text{O}_{12}$) [15–17], which are derivatives of the simple fluorite structure type, exhibit significantly different variations in radiation stability depending on chemical composition, particularly in the binary systems of $\text{A}_2\text{Ti}_{2-x}\text{Zr}_x\text{O}_7$ [10,11,14]. In this study, we have investigated the radiation response of orthorhombic, rare-earth titanates, Ln_2TiO_5 , a very different structure, but one of diverse compositional possibilities.

Rare-earth titanates of Ln_2TiO_5 , with high mechanical strength, thermal stability and chemical resistance, are important materials for nuclear applications. For example, Dy_2TiO_5 has been demonstrated to display improved structural stability when replacing the boron steels and boron

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carbides as neutron absorbers in control rods of Russian thermal neutron reactors [18,19]. Recent studies on thermophysical properties, including thermal expansion and heat capacity of Ln_2TiO_5 (e.g. Dy_2TiO_5 , Gd_2TiO_5 , Eu_2TiO_5), demonstrate their advantages of thermal stability with low swelling at high temperature (up to 1500 K), desired for control rod materials [20,21]. In addition, the nanocluster form of yttrium titanate found its application in oxide-dispersion-strengthened steel when it was dispersed in ferritic alloy. This alloy is considered as the most promising structural material for advanced nuclear systems due to its greatly enhanced creep resistance at high temperature [22,23] and exceptional radiation resistance originating from stabilized oxide nanoclusters ~ 5 nm in size. However, the structure and chemistry of the nanocluster oxides have not been fully understood, remaining one of the challenging scientific issues in nuclear materials research [24,25]. The Y–Ti–O nanoprecipitates dispersed in steel matrix at high density have been suggested as stoichiometric complex oxide phases such as $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2TiO_5 [26–28], along with nonstoichiometric compositions of reduced Y/Ti ratio (ranging from 0.1 to 0.6) [23]. In many cases, complex chemistry, degree of inherent disordering [29] and crystal size of the oxides [30,31] are important factors that affect the radiation behavior of complex ceramics and the interaction of defect accumulation with the steel matrix [25,32]. In order to describe and control the remarkable stability of the strengthening mechanism of complex Y–Ti oxide clusters, an improved understanding of their phase stability and radiation response is necessary.

Three polymorphs (orthorhombic, hexagonal, cubic) exist for Ln_2TiO_5 titanates, depending on the lanthanide cation size and temperature of synthesis [33]. Larger-sized rare-earth cations (La–Sm) lead to an orthorhombic structure ($Pnam$), while smaller-sized rare-earth cations (Er–Lu, Sc) have a cubic structure ($Fd3m$), which is close to pyrochlore $\text{Ln}_2\text{Ti}_2\text{O}_7$ [34]. The compounds Ln_2TiO_5 with intermediate rare-earth series (Eu–Ho and Y) exhibit polymorphism: in addition to the above two structures, there is a hexagonal structure ($P6_3/mmc$) in which the cations are partially disordered. The orthorhombic structure forms at low temperatures; the hexagonal structure forms at intermediate temperatures; the cubic structure, at high temperatures. For instance, orthorhombic Y_2TiO_5 is stable below 1300 °C, hexagonal Y_2TiO_5 is stable between 1330 and 1520 °C, and an isometric solid solution is stable at higher temperatures. The isometric Y_2TiO_5 has the same structure as pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$, with the Ti site having mixed occupancy and anion deficiencies [35]. The orthorhombic rare-earth titanates have Ti in fivefold coordination with oxygen, forming an off-center square pyramid. Neighboring polyhedra are corner-shared, forming chains parallel to the c -axis. The larger Ln cations are in sevenfold coordination, which is lower than the coordination number of rare-earth cations in the pyrochlore structure (CN = 8). Fig. 1 shows the orthorhombic structure of the larger-sized

lanthanides titanates from La to Dy, including Y. In order to understand the radiation response of these complex, rare-earth titanates, Ln_2TiO_5 , systematic ion-beam irradiation experiments, over a range of chemical compositions, have been completed by in situ and ex situ transmission electron microscopy (TEM) using selected area electron diffraction (SAED) and high-resolution imaging (HRTEM).

2. Experimental details

2.1. Sample synthesis

Polycrystalline Ln_2TiO_5 titanates were synthesized using solid-state reactions from stoichiometrical rare-earth oxides (99.9%) and anatase (TiO_2 , 99.9%) as starting materials. The well-mixed powders were pressed into pellets at room temperature and sintered between 1200 and 1400 °C for 48 h. The structure of the samples was confirmed by powder X-ray diffraction (XRD) and TEM. The unit cell parameters were derived from Rietveld refinements of the observed XRD patterns using the Fullprof program, as described in a previous paper [36].

2.2. Ion beam irradiation

Small particles of rare-earth titanate oxides were dispersed on carbon-coated TEM grids and irradiated by 1 MeV Kr^{2+} ions at temperatures ranging from 50 K (using a Gatan liquid observed intermittently by in situ TEM at the IVEM-Tandem Facility of Argonne National Laboratory). A constant ion flux of 6.25×10^{11} ions $\text{cm}^{-2} \text{s}^{-1}$ was used during all irradiation experiments. Ion range, nuclear and electronic stopping of the 1 MeV Kr^{2+} projectiles were calculated by SRIM 2008 (Table 1). The ion range of ~ 300 nm is greater than the typical size of the thin particles on the TEM grid. Therefore, most of the 1 MeV Kr^{2+} ions passed through the samples, and the effect of implanted impurity atoms by irradiation is negligible. To avoid concurrent electron-beam damage, the electron beam was turned off during ion irradiation. SAED patterns were used to monitor structural transformations intermittently with increasing ion dose. Additionally, high-resolution TEM imaging was employed to characterize structural evolution at the atomic scale. The critical amorphization fluence, F_c , at which complete amorphization occurs, was determined to be the point at which all diffraction maxima in the SAED patterns disappeared.

Several grains on the TEM grids were monitored simultaneously during the irradiation period for statistical measurements for each irradiation temperature. The data were subsequently analyzed to determine the critical temperature, T_c , at which the rate of crystalline recovery is equal to the damage rate, and above which the materials can no longer be amorphized by the irradiation [9]. This temperature is deduced by fitting a direct impact model [4] to the experimentally determined amorphization dose:

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