



Full length article

Thermodynamics of radiation induced amorphization and thermal annealing of Dy₂Sn₂O₇ pyrochlore

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ARTICLE INFO

Article history:

Received 6 April 2018

Received in revised form

5 June 2018

Accepted 8 June 2018

Available online 14 June 2018

Keywords:

Pyrochlore

Irradiation effect

Amorphization

Annealing

Calorimetry

ABSTRACT

Thermodynamics and annealing behavior of swift heavy ion amorphized Dy₂Sn₂O₇ pyrochlore were studied. Its amorphization enthalpy, defined as the total energetic difference between the irradiation amorphized and undamaged Dy₂Sn₂O₇ states, was determined to be 283.6 ± 6.5 kJ/mol by high temperature oxide melt drop solution calorimetry. It has been an enigma that stannate and some other pyrochlores do not follow the general r_A/r_B -radiation resistance relation seen in most pyrochlore systems. In this work, we use the amorphization enthalpy, which reflects all the complex chemical and structural characteristics, as a more effective parameter to correlate the radiation damage resistance of pyrochlores with their compositions. It successfully explains the superior radiation damage resistance of the stannate pyrochlores compared with titanate pyrochlores. Differential scanning calorimetry (DSC) reveals a strong exothermic event starting at 978 K, which is attributed to long-range recrystallization based on X-ray diffraction (XRD) analysis, similar to the effect previously observed in Dy₂Ti₂O₇. A second pronounced heat event beginning at ~1148 K, which results from local structural rearrangement, is clearly decoupled from the first event for irradiated Dy₂Sn₂O₇. Both the heat releases measured by DSC on heating to 1023 and 1473 K, and the excess enthalpies of the annealed samples indicate that the recovery to the original, ordered state was not fully achieved up to even 1473 K, despite XRD showing the apparent restoration of crystalline pyrochlore structure. The remaining metastability may be attributed to local disorder in the form of weberite-like short-range domains in the recrystallized material. Intriguingly, the second event for different pyrochlores generally starts at similar temperatures while the onset of the long range recrystallization is compositionally dependent. The amorphization and thermal annealing behavior observed in irradiated Dy₂Sn₂O₇ may provide insights into the general mechanisms of radiation damage and recovery of pyrochlores relevant to their nuclear applications.

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1. Introduction

Pyrochlore oxides (A₂B₂O₇, *Fd* $\bar{3}m$) possess a (2 × 2 × 2) fluorite (AO₂, *Fm* $\bar{3}m$) derivative superstructure with one eighth of oxygen anions replaced by vacancies and two types of cations (A and B) ordered along the <110> direction [1–4]. The complex chemistry, physical properties [5–7] and their ability to accommodate radionuclides (U, Pu, and fission products) [4,8,9], which vary with their

cation compositions, enable this group of materials to be utilized for various applications including mixed ionic/electronic conducting electrodes [10], catalysts for oxygen generation in Li air batteries [11], nuclear waste forms, and hosts of inert matrix fuels [4,8,9].

Radiation induced amorphization and annealing behavior of pyrochlores are particularly of interest for nuclear applications [12–18], as the resulting structural modifications lead to significant changes in their chemical and physical properties and thus have major influences on the mechanical integrity of materials with pyrochlore as a component [4,9,19–21]. These property changes may adversely affect the long-term reliability of the materials, for instance, degradation of their performance as nuclear waste forms when placed in a geological repository [22,23] or inert matrix fuels

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during nuclear reactor operation [24]. On the other hand, controlled irradiation combined with designed thermal treatment can provide a promising route to generate thermodynamically metastable materials with tailored, desired properties such as high ionic conductivity [10]. Therefore, it is crucial to understand and be able to predict the irradiation behavior and damage recovery during thermal annealing of pyrochlores with different cation compositions.

Previous studies have demonstrated that the amorphization resistance of $A_2B_2O_7$ pyrochlores has a strong correlation to the cation radius ratio (r_A/r_B) [2,5,25]. Kr^{2+} ion beam irradiation coupled with *in situ* TEM observation revealed that the critical amorphization temperature T_c , the temperature above which a material can no longer be amorphized due to dynamic damage recovery of pyrochlores, generally increases (i.e., the amorphization resistance becomes weaker) with larger r_A/r_B [2]. The smaller the ratio r_A/r_B , i.e., the closer the A and B cations in size, the smaller the anti-site defect formation energy and the higher the tendency to accommodate defects by disordering through random mixing of cations [2,5]. Calorimetric studies revealed that the enthalpies of formation are less exothermic for the ordered pyrochlores with smaller r_A/r_B ratios [2,5,25]. The less exothermic formation enthalpy for a specific pyrochlore composition indicates that the ordered and disordered defect-fluorite states are energetically closer and thus the defect formation enthalpy is probably lower as well. As a result, irradiation of the pyrochlores with similar A and B cation sizes will induce atomic disordering into the defect-fluorite structure instead of amorphization. Recent studies on swift heavy ion irradiated $Gd_2Zr_{2-x}Ti_xO_7$ and other titanate pyrochlores illustrated that the radiation damage resistance varies with both B [26] and A [27] cations and the trend follows the expected r_A/r_B behavior. Nevertheless, change of B cation might have a stronger effect than change of A cation, since the B cation directly affects the positional parameter of the 48f oxygen and thus the polyhedral distortions [2].

Despite the general correlations with the disordering tendency, anti-site defect formation energy, and radiation damage resistance, certain pyrochlores, especially stannates, do not follow the r_A/r_B correlations in terms of their defect formation energy and disordering/amorphization resistance [28–31]. Substitution of Ti by larger Sn lowers r_A/r_B but does not induce a higher tendency to disordering, and the defect formation energy actually becomes higher [2,29,30]. In fact, stannate pyrochlores generally have good amorphization resistance, despite their high defect formation energies [2,28–31]. Several previous studies have attempted to explain this anomalous behavior from various points of view, including bonding characteristics and the positional parameter “ x ” of the 48f site oxygen anions [2,32,33]. The x parameter is affected not only by r_A/r_B , but also by cation electronic configurations, metal-oxygen bond character, cation polyhedral geometry, and the degree of framework distortion [2]. These factors have been applied successfully to describe the trend observed in rare earth titanate pyrochlores: the one with the smallest x , $Gd_2Ti_2O_7$, is most susceptible to radiation induced amorphization [2]. Trachenko et al. demonstrated that the materials possessing higher bonding covalency generally exhibit lower resistance to radiation damage [32,33]. In this context, the strong covalent character of Sn-O bonds and the high radiation resistance of stannate pyrochlores still remains enigmatic.

Based on these previous studies, it is evident that amorphization resistance is controlled by a complex interplay between the chemical and structural variations, which cannot be fully described by a single parameter addressed above. Therefore, a more detailed analysis to comprehensively explain the changes in amorphization resistance with composition is highly desirable. From the

thermodynamic point of view, the enthalpy of amorphization, which represents the total energetic difference between the amorphized state and its ordered counterpart, serves as the net energy needed for amorphization or changing the state and the driving force for subsequently thermally induced recrystallization. Therefore, it is reasonable to apply amorphization enthalpy as a general indicator to describe the variation of radiation damage resistance of pyrochlores with different compositions. Recently, machine learning (ML) has been applied to predict the amorphization resistance of pyrochlores [34]. The amorphization energy may serve as a major parameter for such ML calculations.

In this work, swift heavy ion amorphized $Dy_2Sn_2O_7$ was selected as a model stannate pyrochlore for calorimetric studies. This composition was chosen for comparing the observed irradiation behavior with that of the corresponding titanate pyrochlore, $Dy_2Ti_2O_7$, recently investigated using the same approach [18]. Further, $Dy_2Sn_2O_7$ is relatively resistant under low-energy ion irradiation with the damage process dominated by nuclear energy loss (higher displacement per atom (dpa) values needed for amorphization) [29] but yet can still be highly amorphized under swift heavy ion irradiation (mainly electronic energy loss) which is required for studying the amorphization energetics [28]. Using high temperature oxide melt drop solution and differential scanning calorimetry, we determined the enthalpy of amorphization and the energetics of recovery on thermal annealing following our recent approach [18]. The incomplete recovery of short range order despite completed longer-range-recrystallization is consistently observed and is pointed to be a more general phenomenon for pyrochlore oxides.

2. Experimental methods

2.1. Sample synthesis and irradiation

Detailed descriptions on synthesis of the $Dy_2Sn_2O_7$ pyrochlore and swift heavy ion beam irradiation have been reported previously [28]. Briefly, the stoichiometric mixture of the binary constituent oxides were ground and pressed into pellets. The pellets were heated to 1473 K for 20 h, and then reground and heated up to 1673 K for another 20 h. Finally, the pellets were ground again into powder, thoroughly dispersed, and then pressed into milled cylindrical indentations (diameter: 10 mm, depth: 70 mm) in custom-made aluminum sample holders [28] for swift heavy ion beam irradiation, which was performed at the X0 beamline of the GSI Helmholtz Center for Heavy Ion Research in Darmstadt, Germany. A beam of 2.2 GeV Au ions was used which fully penetrated the samples and induced an electronic energy loss across the sample of 46.5 ± 1.2 keV/nm [28]; the nuclear energy loss was neglected, as it was at least three orders of magnitude lower than the electronic energy loss [28]. The sample was homogeneously irradiated to a fluence of 8×10^{12} ions/cm² using a limited flux of 1×10^9 ions/s·cm² to avoid sample heating [28]. Several holders were simultaneously irradiated to obtain ~100 mg of sample, which was then removed from the holders after irradiation and reground into fine powder for later structural and calorimetric characterizations.

2.2. X-ray diffraction

Powder XRD was performed with a Bruker D8 Advance diffractometer for the undamaged, radiation damaged, and DSC annealed (to 1023 and 1473 K after irradiation) $Dy_2Sn_2O_7$ samples. XRD data were acquired from 10 to 100° 2 θ with a step size of 0.01° and a counting time of 1.5 s per step. For each measurement, the intensities of XRD peaks were normalized with respect to its strongest peak to yield the relative intensities of reflections. Peaks-

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