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Phenomenological model for the formation of heterogeneous tracks in pyrochlores irradiated with swift heavy ions

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Abstract

Zirconate and titanate pyrochlores were irradiated with swift heavy ions in order to investigate the effects of the chemical composition on the structural changes induced by high electronic excitation. Both transmission electron microscopy and X-ray diffraction results show that the structural modifications induced by irradiation with 120-MeV U ions are strongly dependent on the sample composition: $Gd_2Ti_2O_7$ is readily amorphized, whereas $Gd_2Zr_2O_7$ is transformed into a radiation-resistant anion-deficient fluorite structure. For $Sm_2Zr_2O_7$, $Eu_2Zr_2O_7$ and $Nd_2Zr_2O_7$, more complex behavior is observed, since both pyrochlore–fluorite phase transformation and amorphization occur. A new phenomenological model (the heterogeneous track overlap model, HTOM), which assumes a direct impact mechanism coupled with a single track overlap process, is proposed to describe the formation of heterogeneous track structures consisting of mixed anion-deficient fluorite and amorphous domains. The pyrochlore composition mainly influences the structure of ion tracks (and weakly their diameter), and essentially concerns the amount of amorphous phase vs the amount of fluorite counterpart.

Keywords: Ion irradiation; Pyrochlores; Phase transformations; X-ray diffraction; Transmission electron microscopy

1. Introduction

The study of irradiation-induced phase transformations in ceramics is of great interest from both fundamental and technological viewpoints. Several phenomenological models were developed to interpret the damage build-up induced by ion irradiation, and they were more particularly applied to the description of the crystalline-to-amorphous phase transformation induced by displacement cascades at low energy where ballistic collisions (S_n) are dominant [1,2]. Among these models, the Gibbons description [1] was frequently used to interpret the effects of S_n induced by low-energy ions. A simplified version of this model (direct-impact process), assuming that one ion impact is sufficient to totally transform the matter inside the cylinder surrounding the ion path, was successfully used to describe the damage accumulation in insulators irradiated with swift heavy ions, where electronic excitation (S_e) overwhelms the ion slowing-down (most of metals and semiconductors being insensitive to S_e) [3–5]. Nevertheless, it should be remembered that the validity of this representation relies on the strong assumption that, above a S_e threshold, all the volume of an ion track is transformed. Actually, transmission electron microscopy (TEM) observations are needed to verify this hypothesis of homogeneous track structure. However, very recently, inhomogeneous track structures have been observed in TEM experiments devoted to the investigation of radiation damage induced by swift heavy ions in a particularly interesting class of insulators: pyrochlore-type oxides with the $A_2B_2O_7$ stoichiometry [4–6].

Ordered $A_2B_2O_7$ pyrochlores belong to the $Fd\bar{3}m$ space group, which is a superstructure of the ideal fluorite

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structure ($Fm\bar{3}$ space group). They have two cation sites, one-eighth fewer anions and a lattice constant twice that of their parent fluorite-like (AO_2) arrangement. The A and B cations occupy the 16c and 16d sites, respectively, and oxygen atoms are located at the 48f and 8b positions (Fig. 1). The anion sublattice can be completed by adding missing oxygen atoms in the 8a site to form the fluorite structure. These oxides exhibit many interesting structural, physical and electrical properties, which have been studied extensively over the past twenty years [7–16]. The variety of pyrochlore chemistry, leading to the remarkable versatility of the physico-chemical properties of these compounds, led to essential technological applications in various domains, such as catalysis, sensors, ionic conductors and thermal barrier coatings [7]. Moreover, owing to the high radiation resistance of some compositions, pyrochlores were considered as potential matrices for the immobilization or transmutation of actinides produced in nuclear power plants [8]. Actually, 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 $Gd_2Zr_2O_7$ to 1.78 for $Sm_2Ti_2O_7$ [7,8].

Although the crystalline-to-amorphous phase transformation induced by low-energy ion irradiation in pyrochlores has drawn much attention in the past [8–16], information concerning the damage due to electronic excitation arising from irradiation with swift ions (hundred mega-electronvolt range) is still incomplete owing to the small number of experiments devoted to this topic [4–6,17,18]. The most complete investigations were performed in $Gd_2(Zr_xTi_{1-x})_2O_7$ (with $0 \leqslant x \leqslant 1$) by Lang et al. [5,6] (irradiations with 1.4-GeV Xe ions), by Patel et al. [17] (irradiations with hundred MeV ions) and by Sattonnay et al. [4,18] (irradiations with 780-MeV Kr ions, 870-MeV Xe ions and 940 MeV-Pb ions). One of the main results is that the susceptibility to radiation-induced amorphization exhibits a systematic decrease with increasing Zr content, as also observed for irradiations performed with low-energy ions. Whereas $Gd_2Ti_2O_7$ is readily amorphized, the end member $Gd_2Zr_2O_7$ is transformed into a radiation resistant anion-deficient fluorite structure upon irradiation at room temperature [4–6,8,9,12]. From these results, it was concluded that zirconates are more radiation resistant than titanates.

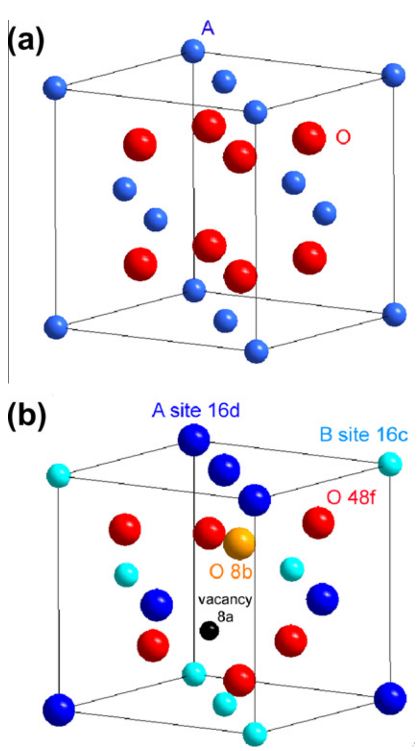

Fig. 1. (a) Fluorite structure and (b) one-eighth of pyrochlore structure.

Observations by TEM of $Gd_2(Zr_xTi_{1-x})_2O_7$ pyrochlores (with $0 \leqslant x \leqslant 1$) irradiated with 1.4 GeV Xe ions showed that the single ion tracks created in the investigated compounds (except for $Gd_2Zr_2O_7$) consist of an amorphous core surrounded by a shell of anion-deficient fluorite structure, which is itself surrounded by a defect-rich pyrochlore region [5,6]. The proportion of fluorite vs amorphous phase depends on x, the degree of substitution of Ti by Zr: it increases with x, and no amorphous phase is observed for $Gd_2Zr_2O_7$. The decrease in the size of the different track zones with increasing Zr content is thus the result of enhanced radiation stability for the Zr-rich pyrochlores [4–6].

The results obtained so far clearly show that an ion track in $Gd_2(Zr_xTi_{1-x})_2O_7$ is not homogeneous, but consists of a mixture of an amorphous part, due to a pyrochlore → amorphous (P → A) transition, and an anion-deficient fluorite part, due to a pyrochlore → fluorite transition (P → F) which occurs simultaneously. Thus, total amorphization is not produced directly in each individual ion track (P → A transition), a second impact into the previously transformed region being at least necessary to entirely transform the material via a fluorite → amorphous transition (F → A). Consequently, the direct impact model cannot be applied in this case.

This paper aims to report: (i) a new phenomenological description (called the heterogeneous track overlap model, HTOM), developed to interpret the phase transformation build-ups occurring in the case where heterogeneous track structures are formed; (ii) a comparative study of the damage created by swift heavy ions in several (titanates or zirconates) pyrochlores, performed to investigate the effects of the chemical composition on the phase transformations induced by swift heavy ions. X-ray diffraction (XRD) and TEM were implemented to determine the structural changes induced by irradiation and monitor the damage build-up in $Gd_2Ti_2O_7$, Gd_2TiZrO_7, $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $Eu_2Zr_2O_7$ and $Nd_2Zr_2O_7$. The new model is applied to interpret the phase transformation build-ups observed experimentally.

2. Heterogeneous track overlap model

The first phenomenological description of damage accumulation in ion-irradiated solids was provided by Gibbons