Phase Stability and Pressure Dependence of Defect Formation in $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ Pyrochlores

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We report dramatically different behaviors between isostructural $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ pyrochlore at pressures up to 44 GPa, in which the substitution of Ti for Zr significantly increases structural stability. Upon release of pressure, the $Gd_2Ti_2O_7$ becomes amorphous. In contrast, the high-pressure phase of $Gd_2Zr_2O_7$ transforms to a disordered defect-fluorite structure. First-principle calculations for both compositions revealed that the response of pyrochlore to high pressure is controlled by the intrinsic energetics of defect formation.

A fundamental understanding of materials response to extreme conditions is of greatest significance in the fields of materials science, nuclear engineering, condensed matter physics and geosciences, and provides the basis for designing and developing advanced materials for a variety of engineering applications. Specifically, phase stability and transformation processes are critical to the development of novel materials utilized in the advanced nuclear energy systems in which the extreme conditions such as high temperature, high pressure, and extremely high radiation fields are encountered.

Pyrochlore, $A_2B_2O_7$, has a wide range of compositions due to its structural flexibility; thus, pyrochlores find application in a surprising number of very different technologies, from use as electrolytes in solid oxide fuel cells to advanced nuclear materials for the immobilization of actinides and as an inert matrix fuel [1–11]. A variety of phase transitions occur in pyrochlore, including the crystalline-to-amorphous transition, phase decomposition and an order-disorder structural transformation [1,3–8]. Dramatically enhanced radiation resistance and ionic conductivity have been observed on substituting Zr for Ti at the *B* site of rare earth element pyrochlores, and this change is closely related to the energetics of disordering of the *A*- and *B*-site cations, as well as disordering of the anion vacancies [6–8]. The isometric pyrochlore structure, $A_2B_2O_7$, is a derivative of the simple fluorite structure, AX_2, but with two different cation sites and one-eighth fewer anions; both cations and anion vacancies are ordered [1]. The pyrochlore structure is unique in that cation and anion sublattices can be disordered independently by thermal treatment and chemical substitution [12]. In pyrochlore, all of the atoms occupy special positions, except for the oxygen at $48f$. Thus, the single positional coordinate, x_{48f}, uniquely defines the structure, such that when x_{48f} equals 0.375, the structure is a perfect defect-fluorite structure. The structural stability of $A_2B_2O_7$ pyrochlores

depends on the ratio of cation radii, r_A/r_B [1]. Energetic ion-beam bombardment can induce phase transformations, in which the ordered pyrochlore structure transforms to a disordered defect-fluorite structure or the amorphous state [3–8]. The irradiation-induced pyrochlore-to-fluorite (order-disorder) transition and amorphization of pyrochlore is controlled by the accumulation of antisite defects (mixed occupancy by A^{3+} and B^{4+}) of the cation sublattice and Frenkel defects (interstitial and vacancy pairs) on the anion sublattice.

Pressure plays an important role in the structural stability of materials that experience order-disorder transformations. Recent studies have reported a phase transformation and amorphization of pyrochlore at extremely high pressures (>50 GPa) [13–15]. However, the mechanisms of the pressure-induced order-disorder transition and amorphization remain unknown. In this letter, we compare, for the first time, pyrochlores under two different extreme conditions: ion-beam irradiation and high pressure. Based on a combination of results obtained by x-ray diffraction, Raman scattering and theoretical calculations, we have found that the pressure-induced phase transition in pyrochlore oxides is controlled by the energetics of defect formation. During release of pressure, the self-amorphization of compressed $Gd_2Ti_2O_7$ and formation of the defect-fluorite structure in $Gd_2Zr_2O_7$ are intrinsic. These results demonstrate that the phase stability and the structural transformation processes of pyrochlore structure are strongly correlated to the energetics of defect formation, and the intrinsic properties (chemical composition and associated structural changes) inherently control the response of pyrochlore to extreme conditions (such as high pressure or an intense radiation field).

The samples of pyrochlore used in this study were polycrystalline with an average grain size of less than 2 μm. High-pressure experiments were completed using a diamond anvil cell (DAC), and pressures were measured

by the ruby-fluorescence method [16]. Although a methanol/ethanol liquid (4:1) was used as a pressure medium in most of the experiments, good quasihydrostatic conditions were obtained because we used a large ratio of pressure medium to sample volume. This was verified by the well-separated fluorescence peaks obtained from the ruby crystal, and the pressure difference measured between different rubies in the chamber was less than 2 GPa at the highest pressure reached. The angle dispersive x-ray diffraction experiments were conducted at the X-17C station of National Synchrotron Light Source, Brookhaven National Laboratory, with monochromatic wavelength beam ($\lambda =$ 0.4066 Å), which was focused to a spot size diameter of $\sim$25 μm. The x-ray diffraction patterns (Debye rings) were first recorded on an image plate and then integrated into two-dimensional patterns using the FIT2D software [17]. The formation energy of cation antisite defects and anion Frenkel defects in $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ pyrochlores at various pressures were calculated using the VASP code [18] based on the refined lattice parameters and atomic coordinates.

Figure 1 shows the XRD patterns of $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ at different pressures. $Gd_2Ti_2O_7$ has the typical pyrochlore structure up to the highest pressure reached (45 GPa, Fig. 1(a)]. However, a broad, weak shoulder appeared in the XRD pattern between the diffraction maxima of {222} and {004} at pressures greater than 32.8 GPa, which indicates that some structural change has occurred. The $Gd_2Zr_2O_7$ pyrochlore is only stable below 23 GPa or even lower (depending on the type of pressure medium). At pressures above 23 GPa, a high-pressure phase forms from $Gd_2Zr_2O_7$ [Fig. 1(b)]. The high-pressure phase and the

pyrochlore structure coexist over a wide pressure range (10–15 GPa). The diffraction peaks of the high-pressure phase are broad at room temperature. The broad diffraction maxima are not due to the pressure medium because similar features were observed when argon or nitrogen pressure media were used, but rather may be attributed to the formation of nanosized domains of the high-pressure phase, as has been confirmed by *ex situ* TEM observations in similar systems [19]. The high-pressure phase may have a structure similar to that of defect-fluorite [20,21], where the cations of Gd^{3+} and Zr^{4+} are disordered on the *A* and *B* sites. The complete transition to the high-pressure (HP) phase was achieved at 44 GPa [Fig. 1(b)]. The pyrochlore-to-HP-phase transition is also an O-D transition, but the high-pressure phase is not well crystallized because the disordering of the cations may not be complete even after the HP phase formed.

The pressures for the transformation from pyrochlore to the HP-phase in the $Gd_2(Ti_{1-x}Zr_x)_2O_7$ binary system are shown in Fig. 2. The substituion of Ti for Zr at the *B* site significantly increases the pressure of the transformation to a high-pressure phase. A very similar relation, as a function of composition, has been discovered in the $Gd_2(Ti_{1-x}Zr_x)_2O_7$ binary system for the change in the critical temperature of the radiation-induced, crystalline-to-amorphous transformation (see inset in Fig. 2) [7,10,22]. In the irradiation experiments, the critical tem-

FIG. 1 (color online). Selected XRD patterns of (a) $Gd_2Ti_2O_7$ and (b) $Gd_2Zr_2O_7$ at various pressures. $Gd_2Ti_2O_7$ sample shows good pyrochlore structure patterns up to the highest pressure of 45 GPa, and only a small amount of disordered phase (or high-pressure phase) appeared in the XRD patterns above 32.8 GPa. A high-pressure phase (marked with black spots) coexists with the pyrochlore structure in $Gd_2Zr_2O_7$ starting at pressure of 17.6 GPa and a pure high-pressure phase is observed above 37.2 GPa.

FIG. 2 (color online). The replacement of Ti at the Zr site significantly increases the critical transition pressure to the distorted high-pressure phase from the ordered pyrochlore structure in the binary system of $Gd_2(Ti_{1-x}Zr_x)_2O_7$. Dramatically different behaviors for the $Gd_2(Ti_{1-x}Zr_x)_2O_7$ system, depending on the chemical compositions, were found for the radiation damage-induced crystalline-to-amorphous structural transformation, that is the critical amorphization temperature, above which materials cannot be amorphized, increases significantly for Ti-rich compositions (inset in Fig. 2) [7,8,10,25].

perature is the temperature above which the material can no longer be amorphized. In this case, the greater the Ti content of the pyrochlore, the higher the critical temperature. In other words, the titanate pyrochlore amorphizes at relatively low doses and the damage persists to high temperatures ($>1000\,°C$). Irradiation causes the titanate pyrochlore to become amorphous. In contrast, the zirconate pyrochlore does not amorphize, but rather it is disordered to the defect-fluorite structure.

Dramatically different behavior between $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ was also seen upon release of pressure. Figure 3 shows the x-ray diffraction images during the pressure loading and unloading. $Gd_2Ti_2O_7$ retains the pyrochlore structure, even at a pressure of 45 GPa, and no significant structural disordering was observed [Fig. 3(b)]. Upon release of pressure, more $Gd_2Ti_2O_7$ pyrochlore was transformed to a structurally disordered (amorphous) state, as evidenced by the disappearance of the Bragg peaks in the diffraction image. Complete amorphization was achieved after quenching and holding the sample at ambient conditions for 5 h; the kinetics are slow for the formation of amorphous $Gd_2Ti_2O_7$ [Fig. 3(d)]. In contrast, no amorphous phase was observed for $Gd_2Zr_2O_7$ after pressure release, and the intermediate high-pressure phase transformed to a disordered, defect-fluorite structure [Fig. 3(g)]. Similar to the amorphization process in $Gd_2Ti_2O_7$, the HP-defect-fluorite phase transition is also a kinetically controlled process and a small amount of the high-pressure phase was still observed after the sample was quenched and kept at ambient conditions for 10 h [Fig. 3(h)].

Amorphization on release of pressure is rare and only found in some semiconducting materials [23,24]. It may be related to phase decomposition; however, the mechanism is not clearly understood. For $Gd_2Ti_2O_7$ pyrochlore, the disordered (or partially disordered) structure is not stable at ambient conditions because of the large size difference between the cations in the A and B sites. If the cation antisite defects in the compressed sample exceed a critical value, the system cannot transform back to the ordered pyrochlore structure upon release of pressure, but instead transforms to the completely amorphous state. In contrast, the high-pressure phase of the $Gd_2Zr_2O_7$ pyrochlore simply forms a disordered-fluorite structure because of the smaller size difference between the A- and B-site cations. This is entirely consistent with the results of high energy irradiations, that is the titanate pyrochlore first forms a disordered, defect-fluorite structure that becomes amorphous at low fluences, some fractions of a dpa. However, the zirconate pyrochlore disorders to a defect-fluorite structure that remains stable to extremely high radiation fluences, >100 displacements/atom [6,7]. One can understand the stability of the disordered, defect-fluorite structure that results from either elevated pressures or ion-beam irradiation of $Gd_2Zr_2O_7$ in terms of the structural adjustments that accompany the change in composition. As the size of the B-site cation increases, the structure tends toward the ideal fluorite structure ($x_{48f} = 0.375$) and the energetics of disordering are low [3,6,8]. This has been confirmed by thermochemical measurements of a variety of rare earth titanate and zirconate pyrochlores [25]. In fact, based on the results of irradiation experiments [26,27], one may predict the effects of high pressure on different pyrochlore compositions, that is hafnate pyrochlores should form the disordered defect-fluorite structure on release of pressure. Thus, the energetics of the defect formation process for different pyrochlore compositions, and hence subtle changes in their structures, significantly influence the response of pyrochlore to elevated pressure and irradiation fields. Cation antisite defects and anion Frenkel defects are created in pyrochlores by energetic ion-beam bombardment [2,3]. The accumulation of the defect pairs drives the pyrochlore-to-fluorite and crystalline-to-amorphous structural transformations. Theoretical calculations indicated that materials with higher cation radius

FIG. 3 (color online). X-ray diffraction images for: $Gd_2Ti_2O_7$ at (a) 22.2 GPa, (b) 45.0 GPa, (c) 0 GPa (recovered sample and measured immediately), (d) 1 bar, 5 h after release of pressure. $Gd_2Zr_2O_7$ at (e) 16.0, (f) 44.0, (g) 0 GPa (recovered sample and measured immediately) and (h) 1 bar, 10 h after releasing pressure.
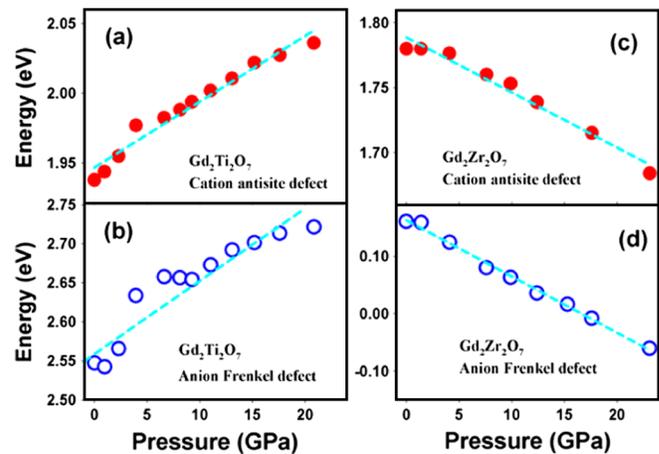
FIG. 4 (color online). Pressure dependence of the calculated formation energies of cation antisite defects and anion Frenkel defects in $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ pyrochlores. Dashed lines are only meant to guide the eyes.

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ratios, and thus a larger deviation from ideal fluorite structure, are more susceptible to irradiation-induced amorphization due to the higher formation energies of cation antisite and anion Frenkel defects [2,3]. The high-pressure phase for $Gd_2Zr_2O_7$ is believed to have a structure compatible with a distorted-defect-fluorite structure [20], and there is only one possible cation site in the unit cell; thus, similar to the results of ion irradiation, pressure will generate antisite defects and anion Frenkel defect pairs in the pyrochlore structure.

In order to gain a more fundamental understanding of the nature of these defects, we have performed quantum mechanical calculations on the formation energies of cation antisite defects and anion Frenkel defects at high pressures. The results reveal different pressure dependences for the defect formation energies in $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ pyrochlores (Fig. 4). At normal pressure, the formation energy of antisite defects in $Gd_2Ti_2O_7$ is greater than in $Gd_2Zr_2O_7$ because of their different A-site to B-site cation radius ratios. These results are in general agreement with those in the literature [3], which were calculated using interatomic potential models. For $Gd_2Ti_2O_7$, the formation energies of the cationic antisite defects and anion Frenkel defects are comparable [Figs. 4(a) and 4(b)], and both increase with pressure. In contrast, the formation energy of anion Frenkel defects in $Gd_2Zr_2O_7$ is approximately one-order of magnitude lower than the corresponding energy for cationic antisite defects, and both show a nearly linear decrease with increasing pressure [Figs. 4(c) and 4(d)]. These calculations suggest that the anion Frenkel defects in $Gd_2Zr_2O_7$ are easily formed, and the ordered pyrochlore structure has a strong propensity to transform to the disordered-fluorite structure at high pressures. The higher defect formation energy of $Gd_2Ti_2O_7$ suggests that this composition will not easily relax back to the pyrochlore structure once defects are formed by either high-pressure or ion irradiation. The theoretical calculations are also consistent with the pressure-induced structural disordering and amorphization in $Tb_2Ti_2O_7$ pyrochlore as reported by Kumar *et al.* [15]. In addition, there is a plateau for the formation energy of anion Frenkel defects in pyrochlore $Gd_2Ti_2O_7$ at pressures between 5 and 10 GPa, indicating that subtle structural adjustments may occur at these pressures. This may be related to a possible structural distortion observed in the system of $Gd_2Ti_2O_7$ [28] and a pressure-induced crystallization of spin liquid in a similar pyrochlore oxide, $Tb_2Ti_2O_7$, at 8.6 GPa [29].

In summary, we report a consistent trend in the phase stability and structural transformation processes for isostructural titanate and zirconate pyrochlores at high pressures and in high radiation fields. Pyrochlore compositions that can accommodate disordering are resistant to forming an amorphous phase at high pressures or high irradiation fluxes. The response of such structures to extreme environments, such as high pressures or irradiation fields, is di-rectly related to the energetics of the disordering process. The performance of materials in extreme environments can be much improved by a consideration of the atomic-scale disordering mechanism and energetics.

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