Phase transition and water incorporation into $\text{Eu}_2\text{Sn}_2\text{O}_7$ pyrochlore at high pressure

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Abstract

Structural changes of europium stannate pyrochlore, $\text{Eu}_2\text{Sn}_2\text{O}_7$, have been investigated at high pressures with *in situ* Raman spectroscopy, photoluminescence (PL), and synchrotron x-ray diffraction (XRD) techniques. The XRD measurements suggest that a pressure-induced phase transition starts at 34.4 GPa. The PL spectrum from Eu^{3+} cations also suggests a phase transition above 36 GPa. XRD analysis shows that the unit cell of the cubic phase deviates from the equation of state at pressures above 23.8 GPa. This is due to the incorporation of water from the pressure medium in the structure at high pressures, which is confirmed by optical spectroscopy measurements.

Introduction

The ternary oxides with general formula of $A_2B_2O_7$ and the isometric pyrochlore structure have been studied extensively over the past decades [1-5] because of their unique structural characteristics and interesting physical properties. There are two cationic sites ($16c$ and $16d$) and two anion sites ($8b$ and $48f$) in pyrochlore structure (see Fig. 1). The $16c$ sites occupied by smaller cations like Ti^{4+} , Zr^{4+} and Sn^{4+} coordinate with 6 anions forming a corner-sharing octahedral framework. Viewing from the (110) direction, there are channels in the framework and half of the larger cations (usually rare earth elements) on the $16d$ site reside in the channels together with two $8b$ anions. Pyrochlore has very flexible chemical compositions and the O^{2-} at $8b$ site can be replaced with OH^- species in natural pyrochlore. Under certain conditions, the cations in pyrochlore can be disordered over the two sites and form anti-site defects. The anions in pyrochlore can also occupy an interstitial site and form anion Frenkel defects [6, 7]. If both cations and anions in pyrochlore are fully disordered, the oxide will have an anion-deficient fluorite structure $(A/B)O_{1.75}$. The order-disorder transition in $A_2B_2O_7$ pyrochlore is closely related to the ratio of the ionic radii of the cations in the two sites. The coexistence of cation anti-site defects and anion Frenkel defects is the unique structural feature of pyrochlore oxides, which is the origin of the unique properties of pyrochlores, such as high ionic mobility [8-10] and catalytic characters [11, 12].

Due to the similar electronic figuration and size between rare earth elements and actinide elements, some actinide cations can partially replace the large rare earth elements and form very stable and radiation tolerant pyrochlores [13, 14]. Some pyrochlore oxides, such as $Gd_2Zr_2O_7$, are proposed as stable, host phases for nuclear-waste immobilization or as inert-matrix fuels [15-17]. The ordered pyrochlore structure is stable only with appropriate cationic radii and charge

combinations. The proper ratio of cation radii r_A/r_B is 1.46 - 1.8 for the pyrochlore structure [1]. The anion deficient-fluorite structure is favorable when $r_A/r_B < 1.46$. An ordered pyrochlore structure is stable for all the rare earth titanates with $RE_2Ti_2O_7$ composition, except $La_2Ti_2O_7$ which has a layered-perovskite structure. Rare earth zirconates, $RE_2Zr_2O_7$, can crystalize in both pyrochlore and defect-fluorite structures, relating to the size of rare earth elements. $Gd_2Zr_2O_7$ is at the boundary of these two structures. All rare earth elements lighter than Gd with larger size form a disordered pyrochlore structure, and heavier rare earth zirconates form an anion deficient fluorite structure. The degree of disordering in rare earth zirconates with pyrochlore structure usually depends on the thermal history of the synthetic samples. The order-disorder transition in pyrochlore structure can be realized by tuning the chemical composition [18], and by treatment under extreme conditions, such as high temperature [19], high pressure [20-22] and energetic ion irradiation [23-25]. The size of Sn^{4+} in pyrochlore is 0.69 nm, larger than that of Ti^{4+} (0.61 nm), but close to that of Zr^{4+} (0.72 nm), however, similar with rare earth titanates, all rare earth stannates have an ordered pyrochlore structure. Because of the strong covalent bond $\langle Sn-O \rangle$ [26], the ion irradiation experiments [27] revealed that rare earth stannates has a lower critical amorphization dose, which is very different from the radiation resistant zirconates [13, 23, 24]. Previous high pressure experiments on rare earth titanates and zirconates suggest that the pyrochlore structure is not stable at high pressure [28, 29], and an amorphous and a defect-fluorite structure formed for titanates and zirconates [30], respectively. It is interesting to study the structural stability of stannates at high pressure conditions and compare with that of rare earth titanates and zirconates. In this paper, the structure of $Eu_2Sn_2O_7$ is studied at high pressure by XRD and optical spectroscopy.

Experimental methods

$\text{Eu}_2\text{Sn}_2\text{O}_7$ powder sample was prepared by a wet chemical method and subjected to a high temperature annealing (1300 °C, 10 hours). XRD measurement confirms that it is a pure single phase with the pyrochlore structure. Like most rare earth titanates ($\text{RE}_2\text{Ti}_2\text{O}_7$), rare earth stannates ($\text{RE}_2\text{Sn}_2\text{O}_7$) also form a fully-ordered pyrochlore structure, and RE^{3+} cations and Sn^{4+} occupy the *16d* and *16c* sites, respectively. For the high-pressure experiments, a symmetric diamond anvil cell (DAC) with a pair of 300 μm diameter culet diamond anvils was used. A hardened stainless steel gasket was pre-indented to a thickness of ~ 40 μm , then a hole of 100–120 μm was drilled in the center of the gasket by an electrical discharge machine (EDM), which serves as the pressure chamber. Methanol/ethanol (4/1 volume ratio) liquid was used as the pressure-transmitting medium. The *in situ* X-ray diffraction experiments were performed at X17c of National Synchrotron Light Source, Brookhaven National Laboratory with a monochromatic X-ray beam (30.5 KeV energy and beam size of 25×30 μm^2). The Debye images at high pressures were collected with a MAR CCD detector and then integrated into one-dimensional XRD patterns with software Fit2D [31]. Pressure in all the experiments was calibrated with the standard ruby fluorescence method. The unit cell parameters were derived from Rietveld refinement of the measured XRD patterns by using the program Fullprof in the platform of Winplotr [32]. High pressure Raman spectra and photoluminescence spectra were measured in a laboratory facility SPEX-1250M attached with a liquid-nitrogen cooled CCD (Symphony), and a green light from an Ar laser (514.5 nm) was used as the activation light source.

Results and discussions

The structure of $\text{Eu}_2\text{Sn}_2\text{O}_7$ pyrochlore was measured with synchrotron XRD up to 45.8 GPa. Selected XRD patterns at various pressures are shown in Fig. 2. The individual diffraction peaks

from pyrochlore structure are still visible at a pressure of 43.4 GPa, however, some extra peaks began to appear in the XRD pattern at 34.4 GPa, an indication of a pressure-induced phase transition. The strongest diffraction peak from the high-pressure phase is close to the strongest diffraction peak of pyrochlore structure (222), but with a smaller d-value. At 45.8 GPa, the peaks in the pattern are mainly from the high-pressure phase, though some diffraction maxima from the pyrochlore structure did not disappear completely. The transition pressure in $\text{Eu}_2\text{Sn}_2\text{O}_7$ is similar to that in zirconate pyrochlores [28] but with a larger critical transition pressure. To most rare earth zirconate in pyrochlore or defect fluorite structure, the critical transition pressure is less than 30 GPa. The XRD pattern of the high-pressure phase of $\text{Eu}_2\text{Sn}_2\text{O}_7$ is similar with that of the high-pressure phase of zirconate pyrochlore [20, 28-30]. The high pressure experiments for other pyrochlore samples, such as $\text{Gd}_2\text{Zr}_2\text{O}_7$, have shown that the high-pressure phase of pyrochlore is a cotunnite-type structure and the quenched sample has a disordered fluorite structure (Fig. 3c). The normal cotunnite structure has an orthorhombic unit cell and there is only one cationic site with 8-9 coordination of anions. Up to now, all the high-pressure phase of pyrochlores cannot be well fitted with the standard cotunnite structure model. The index of high-pressure phase of $\text{Gd}_2\text{Zr}_2\text{O}_7$ also suggested a monoclinic unit cell. In fact, the cations in pyrochlores cannot be fully disordered by external pressure and some **locally ordered** domain may preserve and the structure of the high-pressure phase is very complicated and thus difficult to be fully identified. To rare earth titanates, because of the large size difference between RE^{3+} and Ti^{4+} , a fully disordering in cation sublattice is impossible. Previous high pressure experiments on $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore has only observed a very broad diffused scattering around the [222] peak at pressures larger than 40 GPa. It is interesting that the disordered structure cannot be quenched to ambient conditions, but the quenched sample became amorphous after the pressure is released (Fig3a).

The XRD measurements showed that the $\text{Eu}_2\text{Sn}_2\text{O}_7$ high-pressure phase is not quenchable and transforms back to the pyrochlore structure after the pressure is released. The structural behavior of $\text{Eu}_2\text{Sn}_2\text{O}_7$ is between rare titanates and zirconates. The critical transition pressure is larger than that of rare earth zirconates, but smaller than that of rare earth titanates. On the other hand, the quenched sample is neither amorphous nor disordered fluorite, but a pyrochlore structure. As it is well known that the order-disorder transition in oxides with pyrochlore structure strongly depends on the size ratio of cations on the A- and B-sites. Fully ordered pyrochlore structure is stable for the systems with larger size ratio, such as in rare earth titanates and stannates. The smaller size ratio ($r_A/r_B < 1.46$) is favorable for the formation of cation anti-site defects and a fully disordered fluorite structure is stable at ambient conditions for the zirconates with rare earth elements heavier than Tb. The external pressure induces the formation of cation anti-site defects even in rare earth titanates and results in severe lattice distortion. Due to the large size difference, however, the severely distorted structure is not stable and the structure is not back to neither ordered pyrochlore nor disordered defect-fluorite structure, but amorphized. Cation anti-site defect is intrinsic to most rare earth zirconates, pressure further enhances the structure disorder, and a fully disordered defect-fluorite structure is stable when pressure is released. The size ratio of cations in stannates is between the corresponding titanates and zirconates, but more close to the latter. The similar cationic size difference between $\text{Eu}_2\text{Sn}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ allows the cations to be partially disordered at high pressures, but the cation disorder in $\text{Eu}_2\text{Sn}_2\text{O}_7$ is not complete and certain degree of order can be preserved in the quenched sample. In addition, the strong covalent bond $\langle \text{Sn-O} \rangle$ is also favorable for the formation of a partially-ordered pyrochlore structure for the quenched sample of $\text{Eu}_2\text{Sn}_2\text{O}_7$.

We refined the XRD profiles of $\text{Eu}_2\text{Sn}_2\text{O}_7$ before the phase transition with the pyrochlore structure model and the P-V curve is plotted in Fig. 4. There is a bump in the curve at pressure of 20-23 GPa, and the P-V curve obviously deviates from Birch-Murnaghan equation of state after 20 GPa. Previous investigations have revealed a similar behavior in the P-V curve of $\text{La}_2\text{Zr}_2\text{O}_7$ [20] and $\text{Sm}_2\text{Zr}_2\text{O}_7$ [28] when methanol/ ethanol pressure medium was used, and it was attributed to the intercalation of water (from ethanol) into the pyrochlore structure. The incorporation of water or hydroxyl in the pyrochlore structure at high pressures may be common in pyrochlore oxides. However, it is difficult to identify the position of water molecule or hydroxyl species in the pyrochlore by x-ray diffraction measurements.

Because of the strong covalent bond $\langle\text{Sn-O}\rangle$, rare earth stannates form a fully-ordered pyrochlore structure. Most rare earth stannates have a good Raman spectrum which is very similar to that of $\text{La}_2\text{Zr}_2\text{O}_7$ [20]. Fig. 5a shows the Raman spectrum of $\text{Eu}_2\text{Sn}_2\text{O}_7$ at different pressures. With the increase of pressure, all the Raman active modes decrease in intensity. Starting at 23.1 GPa, a broad band centered at $\sim 730\text{ cm}^{-1}$ appears in the spectrum. From previous investigations [22, 28, 33], this band comes from the anion disordering in the structure. Raman measurements suggest that the degree of disordering in $\text{Eu}_2\text{Sn}_2\text{O}_7$ is enhanced with the increase of pressure. The mode at $\sim 400\text{ cm}^{-1}$ at ambient conditions is the E_g mode, which contributes to the $\langle\text{Sn-O}\rangle$ vibration. Above 23.1 GPa, this band obviously broadened, which suggested that structural disordering occurred and some Eu cations may share the $16c$ site with Sn^{4+} in the structure. At 45.9 GPa, some extra weak modes are observed, so the pyrochlore structure of $\text{Eu}_2\text{Sn}_2\text{O}_7$ is not stable, and a new high-pressure phase formed. The extra peaks became obvious in the spectrum of $\text{Eu}_2\text{Sn}_2\text{O}_7$ at 49.9 GPa. Based on the comparison of XRD measurements, the new Raman active modes are due to the formation of a cotunnite-type high-

pressure phase. The Raman spectrum of the quenched sample is similar to that of the starting sample, but with much weaker intensities and broader widths. The results indicate that the high-pressure phase is not stable, and the pyrochlore structure is recovered after the pressure has been released. The Raman results are in good agreement with XRD observations. But Raman measurements suggest that some degree of disordering may remain in the quenched sample. As compared with rare earth titanates and zirconates, most rare earth titanates are amorphized after pressure release, while zirconates transform to a fully-disordered fluorite structure. The critical transition pressure of $\text{Eu}_2\text{Sn}_2\text{O}_7$ is between that of rare earth titanates and rare earth zirconates, but the quenched sample has a disordered pyrochlore structure. The stability of the quenched pyrochlore is mainly determined by the ratio of the ionic radii of the cations in the structure. Previous theoretical calculations have shown that the formation energy of defects in titanates is at least one-order magnitude greater than that of the zirconates [7, 20]. Once the defects in titanates have formed at high pressure, the structure cannot change back to the ordered structure when pressure is released due to the large energy barrier for this transition. In the meanwhile, the high-pressure phase is not stable, thus the quenched sample becomes amorphous. Zirconates have a larger cation radius ratio and smaller defect formation energies, thus the disordered-pyrochlore or fluorite structure is stable even at ambient conditions. This explains why most zirconate pyrochlores become a fully-disordered fluorite or a partially-disordered defect-pyrochlore structure after the pressure is released. Rare earth stannate, $\text{Eu}_2\text{Sn}_2\text{O}_7$, is similar in its behavior to the rare earth zirconates, and the quenched stannate is a partially disordered defect-pyrochlore structure.

The pressure dependence of the frequencies of the Raman active modes of $\text{Eu}_2\text{Sn}_2\text{O}_7$ is plotted in Fig. 5b. Because of compression of the structure and shrinkage of the average bond-lengths at

high pressures, all of the Raman active modes increase in frequency with the increase of pressure. However, the slopes of the frequencies show an obvious change at a pressure above 26 GPa. This is due to the cation disordering and the incorporation of water in the pyrochlore. A similar behavior was also observed in $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore at ~ 10 GPa [20]. The water incorporation in pyrochlore oxides may be closely related to the cation disordering in the structure. When smaller cation Sn^{4+} replaced Eu^{3+} and occupies the $16d$ site, the channels in the pyrochlore structure have relatively larger space and smaller molecule or clusters like water or OH^{-1} species have more chance to fit in.

Photoluminescence measurements of Eu^{3+} can be used to investigate crystal field splitting due to the structure. Like other rare earth elements, Eu^{3+} is a common phosphor, and a strong PL spectrum can be observed in the stoichiometric pyrochlore $\text{Eu}_2\text{Sn}_2\text{O}_7$. Fig. 6a shows the light emission spectrum of $\text{Eu}_2\text{Sn}_2\text{O}_7$ at various pressures. The PL spectrum of Eu^{3+} is mainly in the wave number range of $2400 - 4200 \text{ cm}^{-1}$ (wave length: $587.0 - 656.3 \text{ nm}$). The strongest band at 2440 cm^{-1} (588.4 nm) is contributed by $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. The PL spectrum becomes weaker with the increase of pressure. However, above 26.4 GPa, new broad bands appear at around 3480 cm^{-1} (627 nm). When the pressure is increased to 45.9 GPa, two additional bands appear near the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ peak, and the new bands at 627 nm become very strong. The PL spectrum at 49.9 GPa is completely different from that of the starting material, which suggests that the high-pressure phase is fully-formed. The PL spectrum of the new phase is comprised of two bands at 2400 cm^{-1} and 2640 cm^{-1} and several strong bands around 3500 cm^{-1} . The high-pressure phase is not stable after the release of pressure, and the spectrum reverted to its original, low-pressure form. Two broad bands appear in the PL spectrum at $3000\text{-}3500 \text{ cm}^{-1}$ during the release of pressure, and as is evident in the spectrum of the quenched sample. These two bands are very close to the modes

of water in compounds. This provides additional evidence that water or hydroxyl have been incorporated into the pyrochlore structure as a result of the increased pressure. The incorporation of water into the pyrochlore structure occurs above 23-26 GPa. For experiments at pressures up to 20 GPa, followed by quenching, no broad bands were observed in the PL spectrum (Fig. 6b). Based on XRD, Raman and PL measurements, the incorporation of water into the pyrochlore structure is associated with cation disordering. The water comes from the pressure medium because we used the ethanol always containing wt.5% water.

Conclusions

$\text{Eu}_2\text{Sn}_2\text{O}_7$ pyrochlore was investigated at high-pressure with an ethanol/methanol pressure medium. *In situ* XRD results suggest that the pyrochlore structure is unstable at high-pressure and starts to transform to a cotunnite-type high-pressure structure at 34.4 GPa. The high-pressure phase is not quenchable, and the recovered $\text{Eu}_2\text{Sn}_2\text{O}_7$ is a disordered pyrochlore. The P-V curve clearly deviates from Birch-Murnaghan equation of state above 23 GPa. Both XRD, Raman and PL spectrum measurements indicate that water from the pressure medium is incorporated into the pyrochlore structure at 23-26 GPa at the same time that cation disorder is initiated.

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Figure Captions

Fig. 1 The crystal structure of $A_2B_2O_7$ pyrochlore as viewed along the $\langle 110 \rangle$ direction. The network of corner-shared octahedra is built with B_2O_6 units, and the tunnels of the network are occupied by one $16d$ cation (larger sphere) and two $8a$ anions of oxygen or hydroxyl.

Fig. 2 XRD profiles of $Eu_2Sn_2O_7$ at high pressures. Extra diffraction peaks from the cotunnite-type high-pressure phase are marked with arrows and start to appear at 34.4 GPa.

Fig. 3 The comparison of XRD patterns between (a) $Gd_2Ti_2O_7$, (b) $Eu_2Sn_2O_7$ and (c) $Gd_2Zr_2O_7$. The first row shows the XRD pattern of samples at lower pressures without structural changes; The second row shows the patterns of samples at the highest pressure we reached. $Eu_2Sn_2O_7$ and $Gd_2Zr_2O_7$ are nearly pure high-pressure phase, while $Gd_2Ti_2O_7$ is still pyrochlore structure with a broad diffuse scattering near the strongest peak (222) of the pyrochlore structure; The third row is the XRD profiles of the quenched samples. $Gd_2Ti_2O_7$ is nearly fully amorphous, $Eu_2Sn_2O_7$ recovered to the pyrochlore structure, and $Gd_2Zr_2O_7$ is a mixture of the high-pressure phase and the defect fluorite.

Fig. 4 The pressure dependence of the unit cell volume of $Eu_2Sn_2O_7$. An abnormal change of the unit cell volume was observed above 23.8 GPa, which is related to the water insertion into the pyrochlore lattice.

Fig. 5 (a) Raman spectrum of $Eu_2Sn_2O_7$ at high pressures; (b) Frequency dependence of the observed Raman active modes with pressure. The Raman signal becomes very weak at high pressure, and a broad band due to disordering appeared in the spectrum between $700-800\text{ cm}^{-1}$. The dashed lines are linear fit for the wavenumbers of the modes. Slope of the frequency-pressure for all the Raman active modes has a discontinuous change at approximately 26 GPa.

Fig. 6 (a) Photoluminescence measurement of $\text{Eu}_2\text{Sn}_2\text{O}_7$ shows that several bands begin to appear at around 3500 cm^{-1} (627 nm) and become stronger in the high-pressure phase above 45.9 GPa; (b) Comparison of the full spectrum (Raman and photoluminescence) of the initial sample and the samples quenched from 20 GPa and ~ 50 GPa. The latter has an obvious broad band around $2800 - 3600\text{ cm}^{-1}$, which is due to the water or hydroxyl incorporation into the pyrochlore structure.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6