Structural Stability of Pyrochlore Manganate In$_2$Mn$_2$O$_7$ Under High Pressure

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The pyrochlore manganate In$_2$Mn$_2$O$_7$ is a very promising ferromagnetic semiconductor material, which has a good application prospect in spin transport due to its very low electron effective mass, high Curie temperature, and structural stability. In this paper, In$_2$Mn$_2$O$_7$ with pyrochlore structure was successfully prepared by high temperature and high pressure combined with the sol–gel method, and the in situ high-pressure X-ray diffraction experiment was carried out on it. The results showed that the structure of In$_2$Mn$_2$O$_7$ was very stable in the pressure range of 0–29.0 GPa, and its bulk modulus was given. This lays a foundation for the application of In$_2$Mn$_2$O$_7$ in extreme environments.

Keywords: pyrochlore, manganate, high pressure, high temperature, structural stability

INTRODUCTION

In the past decades, there has been increasing interest in the pyrochlore oxide materials (general formula A$_2$B$_2$O$_7$) for the studies in both basic science [1, 2] and engineering [3]. Due to the tetrahedral geometry of cations in pyrochlore, very rich quantum phenomena were discovered recently. For example, Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ are Ising pyrochlore materials with Ising anisotropy and effective antiferromagnetic exchange interaction [4]. They have classical spin-ice ground state, and the magnetic moment at each tetrahedral vertex forms a two-in and a two-out degenerate distribution. Besides, the anomalous Hall effect is found in Nd$_2$Mo$_2$O$_7$ [5], the giant magnetoresistance in Ti$_2$Mn$_2$O$_7$ [6], and the topological state in A$_2$Ir$_2$O$_7$ [7].

Materials combining semiconductivity and magnetism open up possibilities for novel electronic devices that utilize electron spin in addition to charge degrees of freedom [8, 9]. The ferromagnetic semiconductor has attracted special attention because of its spin polarization transport potential in spintronics. A closely related important technical phenomenon is spin filtering, which can be achieved by using ferromagnetic semiconductors as tunneling barriers to generate high spin polarization currents [10, 11]. Ferromagnetic semiconductors used in spintronics are mainly based on magnetic impurities embedded in conventional non-magnetic semiconductors [12]. The robustness of carrier-induced ferromagnetism is very sensitive to the growth conditions and processing methods. The origin of room-temperature ferromagnetism of doped magnetic semiconductors is still a controversial topic. In contrast, undoped magnetic semiconductors exhibit long-range magnetism independent of external doping. At present, some undoped ferromagnetic semiconductors have been reported, mainly including halide CrBr$_3$ [13], CrI$_3$ [14–16], Mn-based pyrochlore oxide [17], perovskite oxide BiMnO$_3$ [18], CuSeO$_3$ [19], and YTiO$_3$ [20]. The ferromagnetic semiconductor most studied in spintronics is europium chalcogenide compound EuX (X = O, S, Se) [10, 21–24]. EuX has good performance in spin filter devices, but the Curie temperature is very low [e.g., Tc(EuO) = 69 K [25]], which is a characteristic of most ferromagnetic semiconductors currently known. In addition, the electronic structure of ferromagnetic...
semiconductors needs to be adjusted in the context of spin transport. The electron injection efficiency is determined by the exchange splitting of the conduction band, and low electron effective mass is the key to achieve high carrier mobility. Similarly, exchange splitting is also important for spin filtering because it produces spin-dependent tunneling current barriers.

Therefore, the combination of strong ferromagnetism and attractive semiconductor properties in a material is ideal, but it is still an issue that needs further study. Wei Chen et al. searched for undoped ferromagnetic semiconductors through high-throughput computational screening [26]. They found that magnetic pyrochlore oxide In$_2$Mn$_2$O$_7$ has a good application prospect in spin transport due to its very low effective electron mass, large exchange splitting of conduction band, stability in air, and high Curie temperature of 130 K. Therefore, the study of the structural stability of In$_2$Mn$_2$O$_7$ under high pressure is of great significance for the application of it under extreme conditions. In this paper, we have successfully synthesized pyrochlore In$_2$Mn$_2$O$_7$. The structural stability In$_2$Mn$_2$O$_7$ has been investigated by angle-dispersive synchrotron X-ray powder diffraction at high pressures.

**EXPERIMENT**

**Sample Preparation**

In this experiment, In$_2$Mn$_2$O$_7$ was synthesized by the sol–gel method combined with the high-temperature and high-pressure (HTHP) method. In$_2$O$_3$ (99.99% purity), MnO (99.9% purity), citric acid (AR: analytical reagent), and nitric acid (AR) were used as raw materials. In$_2$O$_3$ and MnO with the molar ratio of 1.2 were dissolved in nitric acid and diluted in distilled water. Citric acid was then added as a fuel to the above solution to yield a citrate/nitrate ratio of 1.2. The mixed solution was continuously stirred using a magnetic agitator. The solution was evaporated by heating at 150°C until a brown sticky gel was formed. Subsequently, the gel was dried at a temperature up to 200°C. The dried gel was calcined at 500°C in air for 10 h.

Next, the target product was synthesized by the cubic anvil HPHT apparatus. The powder was pressed into cylindrical samples with a diameter of 6 mm and a height of 2.3 mm. The cylindrical sample was put into the sample synthesis chamber with a specific combination, and the chamber was put into the cubic anvil HPHT apparatus (SPD6×600) [27, 28]. The temperature was raised to 1,300°C, and the pressure was increased to 5 GPa. The heat and pressure preservation time was 60 min. At last, we made the temperature drop rapidly to 600°C at a rate of 1°C/s, and then we made the pressure drop to 0 GPa. The sample was then transferred to an argon atmosphere via a glove box.

**X-Ray Diffractometry**

In the ambient condition, the phase purity was detected by powder X-ray diffraction (XRD) measurements using a Rigaku Rotaflex X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å) at room temperature. The test voltage was 40 kV, the current was 30 mA, the scanning range was 10–90°, and the scanning speed was 4°/min. The high-pressure angle-dispersive XRD patterns were collected at the beamline X17C of the National Synchrotron Light Source at Brookhaven for In$_2$Mn$_2$O$_7$ with a monochromatic wavelength of 0.4112 Å. A diamond anvil cell (DAC) with an anvil cut of 300 μm diameter was utilized to generate high pressure with the T301 stainless steel as the gasket, which was pre-indented to a 50 μm thickness. One piece of the as-prepared samples, a small piece of ruby as the pressure calibrant [29], and a 16:3:1 methanol/ethanol/water mixture as the pressure-transmitting medium were loaded into the diamond anvil cells. The distance between the sample and the detector and parameters of the detector were calibrated using a CeO$_2$ standard. All the diffraction data were collected using an MAR CCD detector, and the diffraction profiles were obtained via the radial integration of the two-dimensional diffraction rings using FIT2D software [30]. Rietveld analyses were performed with the software GSAS [31].

**RESULTS AND ANALYSIS**

**XRD Analysis**

The structure of In$_2$Mn$_2$O$_7$ was determined by Rietveld refinement, shown in Figure 1A. The red, blue, and black lines in the figure represent the experiment curve, the calculation curve, and the difference between them, respectively. The green vertical line represents the fitted peak position. From the fitted results, it was determined that the compound In$_2$Mn$_2$O$_7$ crystallized in the cubic system, with the space group Fd-3m (No. 227) and cell parameters a = 9.7113(5)Å, V = 915.8(6)Å$^3$, and Z = 8. In$_2$Mn$_2$O$_7$ can be formulated as In$_2$Mn$_2$O$_6$O', with Mn ions at 16c, In ions at 16d, O at 48f, and O' at 8h. In ions formed twisted cubes with surrounding oxygen atoms, and Mn ions formed twisted octahedrons with surrounding oxygen atoms. It was worth noting that there was only one adjustable position parameter in this structure, which was the x coordinate of the oxygen atom at the position of 48f. Figure 1B is the schematic diagram of its structure. The refinement parameters of the cubic phase In$_2$Mn$_2$O$_7$ structure are given in Table 1.

**In Situ High-Pressure X-Ray Diffraction**

The in situ XRD patterns of In$_2$Mn$_2$O$_7$ at various pressures up to 29.0 GPa have been collected, and a few representative patterns are shown in Figure 2. The results showed that, in the whole pressure range of this experiment, there was no obvious change in the high-pressure XRD diffraction pattern, and there appeared no new diffraction peak. The diffraction peak under each pressure point moved to a higher angle with increasing pressures, accompanied by the weakening of the intensity of diffraction peak, which was usually caused by the increase of lattice disorder under pressure. This indicated that the cell volume of In$_2$Mn$_2$O$_7$ decreased gradually in the test pressure range of 0–29.0 GPa. After releasing the pressure, the positions of diffraction peaks were almost the same as those before pressure rise. The above two points indicated that the cubic phase In$_2$Mn$_2$O$_7$ exhibited excellent structural stability in the whole pressure range in this experiment. When the pressure increased gradually, the compound had no structural phase transition but only slightly
strained, and this change disappeared completely after the pressure was removed. In order to further study the change of the crystal structure of In$_2$Mn$_2$O$_7$ with pressure, Rietveld analyses were performed with the software GSAS under various pressures. We obtained the lattice constants given in Table 1 and volumes under different pressures as shown in Figure 3.

The P–V data were fitted using the Birch–Murnaghan (B–M) equation of state [32], expressed as follows:

$$P = \frac{3.0}{2} B_0 \left[ \left( \frac{V_0}{V} \right)^\frac{7}{2} - \left( \frac{V_0}{V} \right)^\frac{5}{2} \right] \times \left[ 1 + \frac{3}{4} (B'_0 - 4) \times \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right],$$  

(1)

where $B_0$ represents the bulk modulus at zero pressure, $B'_0$ represents the first derivative of the bulk modulus, and $V_0$ represents the volume of a single cell at zero pressure. Taking $B'_0 = 4$, the fitting results are shown as the red curve in Figure 3. It can be seen that the red curve fitted very well with the experimental data within the experimental pressure range, and the fitting results showed $B_0 = 240(4)$ GPa. In addition, when $B'_0$ was not fixed as 4, we obtained $B = 221(6)$ GPa and $B'_0 = 5.5(1.2)$, shown with the fluorescent green dotted line in Figure 3.

This result was compared with the bulk moduli of other A$_2$B$_2$O$_7$ pyrochlore oxides. The bulk moduli of A$_2$Ti$_2$O$_7$ (A = Ho, Y, Tb, Sm) compounds were 213(2), 204(3), 199(1), and 164.8(1.5) GPa [33, 34], and the bulk moduli of A$_2$Sn$_2$O$_7$ (A = La, Eu) compounds were 180(6) and 170 GPa, respectively [35]. It can be seen that the bulk modulus of In$_2$Mn$_2$O$_7$ was obviously larger than that of the above compounds. However, we also studied

| Pressure (GPa) | Lattice parameter (Å) |
|---------------|----------------------|
| 0.6           | 9.6983(7)            |
| 1.6           | 9.6786(4)            |
| 3.2           | 9.6474(3)            |
| 5.0           | 9.6296(2)            |
| 6.2           | 9.6087(7)            |
| 7.4           | 9.5892(2)            |
| 9.5           | 9.5707(1)            |
| 10.8          | 9.5579(2)            |
| 12.4          | 9.5390(3)            |
| 14.0          | 9.5286(6)            |
| 15.5          | 9.5102(1)            |
| 17.3          | 9.4937(2)            |
| 19.4          | 9.4788(4)            |
| 21.0          | 9.4517(5)            |
| 22.9          | 9.4368(5)            |
| 27.0          | 9.3993(3)            |
| 29.0          | 9.3764(2)            |

Note: $R_{wp}$ and $R_p$ as defined in GSAS [29].

**TABLE 1** | Refined atomic coordinates of In$_2$Mn$_2$O$_7$ at ambient condition and lattice parameters at various pressures.

| Atoms | Wyckoff ($x \ y \ z$) |
|-------|-----------------------|
| In    | 16d (0.5 0.5 0.5)     |
| Mn    | 16c (0 0 0)           |
| O(1)  | 48f [0.125 0.125 0.3241(9)] |
| O(2)  | 8b (0.325 0.325 0.325) |

Residuals $^\dagger$ (%)

$R_{wp}$: 6.27%

$R_p$: 5.08%

*FIGURE 1* | (A) Rietveld full-profile refinement of the diffraction patterns of In$_2$Mn$_2$O$_7$ at ambient condition. Red, blue, and black solid lines represent experimental, calculated, and residual patterns, respectively. Vertical markers show the calculated peak positions. (B) A schematic representation of the crystal structures of pyrochlore-type In$_2$Mn$_2$O$_7$.

*FIGURE 2* | Angle-dispersive XRD patterns of In$_2$Mn$_2$O$_7$ at selected pressures with a monochromic wavelength of 0.4112 Å at room temperature. The top red pattern was taken from the samples after the release of pressure.
Within the range of our study, it can be seen that $x_{48f}$ has no sudden change, which also indicates the structural stability of pyrochlore $\text{In}_2\text{Mn}_2\text{O}_7$.

### CONCLUSION

In this paper, the manganate $\text{In}_2\text{Mn}_2\text{O}_7$ was successfully prepared by the sol–gel method combined with high temperature and high pressure. Through XRD characterization at atmospheric pressure, $\text{In}_2\text{Mn}_2\text{O}_7$ was identified as a pyrochlore structure, and its exact crystallographic data and structural refinement parameters were given. Through in situ high-pressure X-ray diffraction, it was found that $\text{In}_2\text{Mn}_2\text{O}_7$ had no structural phase transition below 29.0 GPa, showing excellent structural stability. By fitting the P–V curve with the Birch–Murnaghan (B–M) equation of state, the bulk modulus of the sample was obtained as 240(4) GPa. This lays a foundation for the application of $\text{In}_2\text{Mn}_2\text{O}_7$ in extreme environments.

### DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, and further inquiries can be directed to the corresponding authors.

### AUTHOR CONTRIBUTIONS

XW contributed to the conception and design of the study and completed the high-pressure part of the experiment. HL completed sample synthesis. HL and SM performed the design of figures and wrote the first draft of the manuscript. JY organized the literature. All authors contributed to manuscript revision and read and approved the submitted version.

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