A comparative study of high-pressure behaviors of the two polymorphs of Ho$_2$Ge$_2$O$_7$

Hui Li, Nana Li, Pinwen Zhu and Xin Wang

Two polymorphs of polycrystalline Ho$_2$Ge$_2$O$_7$, one with tetragonal structure and the other with cubic structure, were synthesized by using different methods. The structural stabilities of these two polymorphs under high pressure were investigated by angle-dispersive X-ray diffraction (ADXRD). Pressure-induced amorphization was found in the tetragonal Ho$_2$Ge$_2$O$_7$, which is suggested to be associated with the breaking-up of long chains of the edge-shared polyhedron group Ho$_4$O$_{20}$. By contrast, cubic Ho$_2$Ge$_2$O$_7$ is stable at high pressures up to 33.3 GPa.

1. Introduction

Spin ice has proven to be one of the most fruitful marriages of theoretical and experimental condensed matter physics. It is a remarkable magnetic ground state that can arise in geometrically frustrated pyrochlores, A$_2$B$_2$O$_7$, when magnetic rare-earth ions are situated on the vertices of a lattice of corner-sharing tetrahedra. Competing nearest-neighbor and long-range dipolar interactions result in a short-range ordered ground state for each tetrahedron in which two spins point in and two spins point out. The spin-ice state was first observed in Ho$_2$Ti$_2$O$_7$ by Harris et al. in 1997 since that time, spin ices have been a subject of active experimentation, allowing theorists to come a long way towards understanding this remarkable ground state. Despite significant interest in this class of compounds, only a handful of spin-ice materials have been discovered to date, including the titanates A$_2$Ti$_2$O$_7$, the stan-nates A$_2$Sn$_2$O$_7$, and, more recently, the germanates A$_2$Ge$_2$O$_7$. Recently, the observation of emergent monopole excitations which have captured the attention of the broader scientific community have made spin-ice materials more intriguing. Ho$_2$Ge$_2$O$_7$, a member of the rare-earth pyro-germanate series A$_2$Ge$_2$O$_7$, has been attracting extensive interest because it was found to be a new highly correlated spin-ice material with the highest density of monopoles in the Ho series at low temperatures, and the best natural candidate for monopole studies.

From a structural point of view, rare-earth pyrogermanates A$_2$Ge$_2$O$_7$ possess a variety of crystal structures under ambient conditions, such as triclinic phase for Ln = La, Pr, Nd–Gd, tetragonal phase for Ln = Gd–Lu, and monoclinic phase for In$_2$Ge$_2$O$_7$ and Sc$_2$Ge$_2$O$_7$. Moreover, depending on the synthesis method, different structural modifications of Ln$_2$Ge$_2$O$_7$ can be obtained. By conventional solid state synthesis, Ho$_2$Ge$_2$O$_7$ has the tetragonal structure. However, the cubic phase of Ho$_2$Ge$_2$O$_7$ can be synthesized by the high-pressure and high-temperature (HPHT) method. Therefore, pressure is an important weapon in a researcher’s arsenal for exploring phase space. Pressure is also used to drive materials into new electronic states. Under high pressure, some materials become superconductors, others undergo magnetic phase transitions, and others undergo metal–insulator phase transitions. In magnetic pyrochlore oxides, pressure has been shown to freeze the spin-liquid ground state of Tb$_2$Ti$_2$O$_7$. So, studies on the stability of Ho$_2$Ge$_2$O$_7$ under high pressure are particularly important to understand its exotic magnetic phenomenon.

In this work, we successfully synthesized the two types of Ho$_2$Ge$_2$O$_7$ using different methods. The structural stabilities of these two polymorphs of Ho$_2$Ge$_2$O$_7$ were investigated by angle-dispersive synchrotron X-ray powder diffraction (ADXRD) at high pressures. Pressure-induced amorphization was found in the tetragonal Ho$_2$Ge$_2$O$_7$. Meanwhile, the cubic Ho$_2$Ge$_2$O$_7$ was stable up to the highest pressure tested.

2. Experimental section

Synthesis
The tetragonal Ho$_2$Ge$_2$O$_7$ was synthesized by standard solid state reaction method. High purity oxides of Ho$_2$O$_3$ (99.99%, powder) and GeO$_2$ (99.99%, powder) were used as the starting materials. The raw materials with nominal compositions of Ho$_2$Ge$_2$O$_7$ were uniformly mixed in an agate mortar. The powder obtained was pressed into small pellets and then calcined at 1373 K in air for 12 h. The cubic Ho$_2$Ge$_2$O$_7$ was synthesized by the HPHT method. The as-prepared powders were loaded into a cubic anvil HPHT apparatus (SPD-6 × 600) at
a temperature of 1573 K and a pressure of 5.2 GPa with a holding time of 15 min.

Characterization

Under ambient conditions, the crystal phase structures of the synthesized samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/max-2500 with Cu Kα radiation (λ = 1.54056 Å) in the range 2θ from 10° to 90° at a scanning rate of 4°·min⁻¹. The high-pressure angle-dispersive XRD patterns for the two types of Ho₂Ge₂O₇ were collected at beamline 4W2 of the Beijing Synchrotron Radiation Facility, using a monochromatic wavelength of 0.6199 Å. A diamond-anvil cell (DAC) was utilized to generate high pressure, using a T301 stainless steel gasket which was pre-indented to 50 μm thickness. One piece of the as-prepared samples, a small piece of ruby as the pressure calibrant and a 16 : 3 : 1 methanol/ethanol/water mixture as pressure-transmitting medium were loaded into the diamond-anvil cells. The experimental parameters, including the distance between sample and detector, were calibrated using CeO₂ standard reference material. FIT2D software was employed to convert the image plate records into intensity versus diffraction angle 2θ patterns. Rietveld analyses were performed with the software GSAS. The refinement parameters were the lattice constants, the atomic position of oxygen, a Chebyshev polynomial background, pseudo-Voigt profile parameters, a common isotropic thermal parameter for all atom sites and an overall intensity scaling factor.

3. Results and discussion

Crystal structures under ambient conditions

The observed and calculated XRD patterns of the two types of Ho₂Ge₂O₇ together with their differences are shown in Fig. 1. The diffraction peaks in Fig. 1a match well with the tetragonal structure Ho₂Ge₂O₇ (S.G. P₄₁₂₁₂, no. 92) and the obtained cell parameters are: \( a = b = 6.8041(1) \) Å, \( c = 12.3734(1) \) Å, \( V = 572.83(1) \) Å³ with \( Z = 4 \). In this kind of crystal structure, each Ho³⁺ ion is coordinated to seven oxygen atoms. The Ge₂O₇ unit consists of two tetrahedra (GeO₄) joined by a bridging oxygen atom. The bridging oxygen atoms of the Ge₂O₇ unit do not coordinate to the Ho³⁺ ion. The coordination polyhedron of the Ho³⁺ ion is a distorted pentagonal bipyramid with the Ho³⁺ ion located nearly in the basal plane. The pentagonal axis is almost parallel to the crystal c-axis. Each Ho₂O₇ polyhedron shares three of its O–O edges with neighboring polyhedra. Schematic illustrations are shown in Fig. 2a and b.

The crystal structure data of the cubic Ho₂Ge₂O₇ were refined by Rietveld analysis of the X-ray powder diffraction data. The

| Compound         | Ho₂Ge₂O₇   | Ho₂Ge₂O₇   |
|------------------|------------|------------|
| Crystal system   | Cubic      | Tetragonal |
| Space group      | \( Fd\bar{3}m \) (227) | \( P₄₁₂₁₂ \) (92) |
| \( a/Å \)        | 9.8974(3)  | 6.8041(1)  |
| \( b/Å \)        | 9.8974(3)  | 6.8041(1)  |
| \( c/Å \)        | 9.8974(3)  | 12.3734(1) |
| Atoms Wyckoff    | (x y z)    | (x y z)    |
| Ho 16d (0.5 0.5 0.5) | 8a (0.8761(7) 0.3413(8) 0.1352(1)) |
| Ge 16c (0 0 0)   | 8a (0.8857(3) 0.1469(9) 0.6199(4)) |
| O(1) 48f (0.3255(10) 0.125 0.125) | 4a (0.8141(5) 0.1859(6) 0.7500(8)) |
| O(2) 8b (0.375 0.375 0.375) | 8a (−0.0319(8) 0.1362(6) 0.6260(2)) |
| O(3) 8a (0.0565(6) 0.3575(4) 0.5886(7)) | 8a (0.6774(3) 0.1254(6) 0.5528(4)) |

Residuals\(^a\)/% \( R_{wp} \): 7.07% \( R_p \): 5.64% \( R_{wp} \): 5.83% \( R_p \): 4.61%

\(^a\) \( R_{wp} \) and \( R_p \) as defined in GSAS.²⁴

Fig. 1 Observed, calculated and difference X-ray powder patterns of Ho₂Ge₂O₇ at ambient pressure: (a) Rietveld refinement for the tetragonal Ho₂Ge₂O₇ and (b) Rietveld refinement for the cubic Ho₂Ge₂O₇.

Fig. 2 Schematic representation of the crystal structures of the tetragonal Ho₂Ge₂O₇ ((a) and (b)) and the cubic Ho₂Ge₂O₇ ((c) and (d)).
observed and calculated XRD patterns along with the difference plot are shown in Fig. 1b. The cubic Ho$_2$Ge$_2$O$_7$ belongs to the $Fd\overline{3}m$ (no. 227) space group with the lattice parameters $a = 9.8974(3)$ Å and $Z = 8$. In this cubic phase, it can be formulated as Ho$_2$Ge$_2$O$_{6}$O’ with the Ge ion site at 16c, Ho at 16d, O at 48f and O’ at 8b. The Ho site (16d) coordination polyhedron is a distorted cube that generally contains larger cations, and the Ge site (16c) is a distorted octahedron. It is worth noting that there is only one adjustable positional parameter $x$ for the O atom at the 48f site. Schematic illustrations of the cubic Ho$_2$Ge$_2$O$_7$ are shown in Fig. 2c and d. In addition, the refined atomic position coordinates of the two polymorphs of Ho$_2$Ge$_2$O$_7$ are given in Table 1.

Pressure-induced amorphization of the tetragonal Ho$_2$Ge$_2$O$_7$

The in situ XRD patterns of the tetragonal Ho$_2$Ge$_2$O$_7$ at various pressures up to 22.5 GPa were collected and a few representative patterns are shown in Fig. 3. As can be seen from Fig. 3a, the pressure-dependent X-ray data do not reveal any new diffraction peaks or peak splitting, which indicates that a typical tetragonal structure remains from ambient pressure up to 13.6 GPa. With further increasing pressure, most of the sharp bands have disappeared at 16.9 GPa and no diffraction peaks can be observed, which suggests the formation of an amorphous phase. After releasing the pressure, pressure-induced amorphization of Ho$_2$Ge$_2$O$_7$ is maintained, which indicates the nonreversible nature of the phase transition. A few small peaks appeared after quenching and holding the sample under ambient conditions for 10 h. The recorded pattern for 10 h after release of pressure is almost identical to that of the original phase of tetragonal Ho$_2$Ge$_2$O$_7$, as shown in Fig. 3b.

Pressure-induced amorphization has been the subject of intense study for the past few years because of its importance in materials science and solid state physics. A pressure-induced amorphization of $\alpha$-NaVO$_3$ was observed by Raman spectroscopy, which involved the tetrahedral VO$_4$ chains breaking up abruptly at the transition pressure. In addition, silicates and metavanadate compounds also have chain structures and are the best examples of amorphous materials. As can be seen in Fig. 2a and b, each HoO$_2$ polyhedron shares three of its O–O edges with neighboring polyhedra. And we can clearly see the four polyhedra (Ho$_1$O$_{7}$, Ho$_2$O$_{7}$, Ho$_3$O$_{7}$, Ho$_4$O$_{7}$) close together. The Ho$_2$O$_7$ polyhedron and Ho$_4$O$_7$ polyhedron share an O3(i)–O3(ii) edge with the four other closest polyhedra. In the crystal structure of Ho$_2$Ge$_2$O$_7$, there is a chain, whose constituent unit (Ho$_4$O$_{20}$) is four edge-shared polyhedrons closely linked. In order to understand the reason for the amorphization, we plotted the variation of bond length with pressure for tetragonal Ho$_2$Ge$_2$O$_7$ (Fig. 4). The bond lengths of Ho–O3(i) and Ho–O3(ii) always remain longer than the other Ho–O bond distance, from ambient pressure to the highest pressure. So the infinite Ho$_4$O$_{20}$ chain is relatively easy to disconnect at this junction. Pressure-induced amorphization of Ho$_2$Ge$_2$O$_7$ is suggested to be associated with the breaking-up of long chains of the edge-shared polyhedron group Ho$_4$O$_{20}$. The tetragonal Ho$_2$Ge$_2$O$_7$ showed long-range order at low magnetic fields, but its behavior was similar to spin-ice freezing in a sufficiently strong magnetic field. Owing to the appearance of pressure-
induced amorphization, we can speculate that the tetragonal 
Ho$_2$Ge$_2$O$_7$ may become paramagnetic under high pressure.

The pressure dependences of the lattice parameters and 
volume of tetragonal Ho$_2$Ge$_2$O$_7$ up to 22.5 GPa are shown in 
Fig. 5. It is shown that the lattice parameters and volume of 
Ho$_2$Ge$_2$O$_7$ decrease smoothly with increasing pressure. In order 
to determine the bulk modulus $B_0$, its pressure derivative $B'_0$, and the molar volume under ambient conditions $V_0$, the 
experimental pressure–volume data of the Ho$_2$Ge$_2$O$_7$ were 
ﬁtted to a third-order Birch–Murnaghan equation of state (Fig. 5c). The 
obtained bulk modulus $B_0$ is 193(4) GPa for the tetragonal 
phase with fixed $B'_0 = 4$.

Structural stability of the cubic Ho$_2$Ge$_2$O$_7$ under high pressure

In situ XRD patterns of the cubic Ho$_2$Ge$_2$O$_7$ were collected up to 
33.3 GPa at room temperature and the representative patterns 
are shown in Fig. 6. No splitting or extra peaks appear in the 
patterns, demonstrating that the cubic phase of the Ho$_2$Ge$_2$O$_7$ 
remains stable within the whole pressure range. In this ordered 
pyrochlore structure, all of the atoms are sited at deﬁned 
positions, except for the O 48f atom. Hence, the degree of 
structural ordering can be determined by varying the x positional 
parameter of the O 48f atom. Previous studies on pyrochlore oxides have revealed that a sudden change of the x 
positional parameter of the O 48f atom occurred in the process of 
pressure-induced structural phase transition. For example, 
there was a rapid decrease of the x positional parameter with 
increasing pressure in Gd$_2$Zr$_2$O$_7$, implying a phase transition; the x-coordinate of the O 48f atom increased dramatically after 
the transformation in Sm$_2$Zr$_2$O$_7$. From our reﬁned results, the x 
parameter for the O 48f atom as a function of pressure, as 
shown in the inset of Fig. 7, does not exhibit any anomaly up to 
the highest pressure employed, indicating the structural 
stability of the cubic Ho$_2$Ge$_2$O$_7$. Recent experimental studies 
have reported that the pyrochlore Ho$_2$Ge$_2$O$_7$ exhibited all the 
distinctive properties of a dipolar spin ice: a small, positive 
Curie–Weiss constant; Pauling zero-point entropy; magnetiza-
tion which saturated to half the magnetic moment; a spin-
freeze transition in the ac susceptibility; and the character-
istic magnetic diffuse scattering of spin ices. The stability of

Fig. 5 The lattice parameters ((a) and (b)) and unit cell volume (c) as a function of pressure for the tetragonal Ho$_2$Ge$_2$O$_7$.

Fig. 6 Selected XRD patterns of the cubic Ho$_2$Ge$_2$O$_7$ with increasing pressure. The cubic structure is stable up to 33.3 GPa.

Fig. 7 Observed $P$–$V$ variation ﬁtted with the third-order Birch–
Murnaghan (B–M) equation of state for the cubic Ho$_2$Ge$_2$O$_7$. The inset shows the pressure dependence of the x parameter for the O 48f atom.
the structure ensures the stability of these excellent properties under high pressure.

The pressure dependence of the unit cell volume of the cubic Ho$_2$Ge$_2$O$_7$ is shown in Fig. 7. The data are fitted by a third-order Birch–Murnaghan equation of state as is the case for the tetragonal Ho$_2$Ge$_2$O$_7$. The obtained bulk modulus $B_0$ is $263(4)$ GPa, quite a bit larger than for other ordered pyrochlore oxide materials. For example, the bulk moduli of A$_2$Ti$_2$O$_7$ (A = Ho, Y, Tb, Sm) were 213(2), 204(3), 199(1) and 164.8(1.5) GPa, respectively. And also for Gd$_2$Zr$_2$O$_7$, the bulk modulus was 186(12) GPa. By comparison, the hardness of the cubic phase in Ho$_2$Ge$_2$O$_7$ is higher than that of the tetragonal phase. The difference in bulk modulus might be due to the differences in structure and cohesive energy among these germanates.

4. Conclusions

In summary, the structural behaviors of two types of Ho$_2$Ge$_2$O$_7$ were studied under high pressure by in situ XRD measurements. Pressure-induced amorphization was found in the tetragonal Ho$_2$Ge$_2$O$_7$, which has a chain structure, and is suggested to be associated with the breaking-up of long chains of the edge-shared polyhedron group Ho$_2$O$_{20}$. By contrast, the cubic Ho$_2$Ge$_2$O$_7$ structure is stable at high pressures up to 33.3 GPa. The bulk modulus of the tetragonal Ho$_2$Ge$_2$O$_7$ was obtained as $B_0 = 193(4)$ GPa, and $B_0 = 263(4)$ GPa was obtained for the cubic phase.

Conflicts of interest

There are no conflicts to declare.

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