In situ neutron diffraction study of the formation of Ho$_2$Ge$_2$O$_7$ pyrochlore at high temperature and pressure

SUPPLEMENTARY INFORMATION

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1. Additional Figures

Figure S1. A comparison of the diffraction patterns from the starting materials in vanadium cans (b) and (d) and in the high-temperature setup (a) and (c). The traces labelled (a) and (b) are from a 1:2 mixture of Ho$_2$O$_3$ and GeO$_2$ and (c) and (d) the Ho$_2$Ge$_2$O$_7$ pyrogermanate. Although an increase in background scattering is evident in (a) and (c), and additional peaks arising from the MgO and graphite from the container can be seen (marked by asterisks), all of the sample peaks are clearly visible.

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Figure S2. X-ray powder diffraction patterns from hydrothermally-produced Ho$_2$Ge$_2$O$_7$ pyrogermanate, (a) as made and (b) after heating at 900 °C for 2 hours. Tickmarks show the allowed reflections for the tetragonal pyrogermanate phase.

Figure S3. Variable temperature X-ray diffraction from hydrothermally-produced Ho$_2$Ge$_2$O$_7$ pyrogermanate. The top and bottom panels show individual diffraction patterns at 50 °C and 900 °C and the contour plot shows diffracted intensity as a function of angle and temperature. No changes are observed across this temperature range.
2. Details of Rietveld refinements

The Rietveld refinements of the recovered samples, that are discussed in section 3.3 of the manuscript, were carried out with the following parameters.

In situ sample:

- 20 variables.
- 3511 datapoints.
- $wRp = 3.72 \%$, $Rp = 2.48 \%$.
- 2 phases: $\text{Ho}_2\text{Ge}_2\text{O}_7$ (19.3 wt%), MgO (80.6 wt%).
- Background function: shifted Chebyshev polynomial with 12 terms.
- Peak profile function: back-to-back exponentials convolved with pseudo-Voigt function (GSAS TOF profile 3). 3 refined terms for each phase (constrained to be equal for both phases).

Precursor sample:

- 20 variables.
- 3511 datapoints.
- $wRp = 5.69 \%$, $Rp = 4.76 \%$.
- 2 phases: $\text{Ho}_2\text{Ge}_2\text{O}_7$ (49 wt%), MgO (51 wt%).
- Background function: shifted Chebyshev polynomial with 12 terms.
• Peak profile function: back-to-back exponentials convolved with pseudo-Voigt function (GSAS TOF profile 3). 3 refined terms for each phase (constrained to be equal for both phases).

3. Equation of state determination

3.1 Pyrogermanate

An example refinement from the equation of state determination is shown in Figure S5 and the tabulated results in Table S1. The refinement used the following parameters:

• 27 variables.
• 3510 datapoints.
• \( w_Rp = 5.52\% \), \( R_p = 6.78\% \).
• 3 phases: \( \text{Ho}_2\text{Ge}_2\text{O}_7 \) (59 wt%), \( \text{NaCl} \) (8 wt%), diamond (33 wt%)
• Background function: shifted Chebyschev polynomial with 17 terms.
• Peak profile function: back-to-back exponentials convolved with pseudo-Voigt function (GSAS TOF profile 3). 3 terms refined for diamond only (this signal arises from the sintered diamond anvils and is very strong).

Table S1. Refined parameters from the determination of the equation of state for holmium pyrogermanate.

<table>
<thead>
<tr>
<th>Load (tonnes)</th>
<th>( V (\text{Å}^3) )</th>
<th>Pressure (GPa)</th>
<th>( \text{Ho}_2\text{Ge}_2\text{O}_7 ) (pyrogermanate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>179.72(5)</td>
<td>-0.029(6)</td>
<td>( a (\text{Å}) \quad c (\text{Å}) \quad V (\text{Å}^3) )</td>
</tr>
<tr>
<td>20</td>
<td>167.54(5)</td>
<td>1.98(2)</td>
<td>6.8122(7) 12.398(2) 575.34(18)</td>
</tr>
<tr>
<td>30</td>
<td>160.26(4)</td>
<td>3.67(1)</td>
<td>6.7440(7) 12.281(2) 558.56(17)</td>
</tr>
<tr>
<td>40</td>
<td>156.18(4)</td>
<td>4.83(1)</td>
<td>6.7248(7) 12.249(2) 553.94(17)</td>
</tr>
<tr>
<td>50</td>
<td>151.09(4)</td>
<td>6.54(2)</td>
<td>6.6987(8) 12.205(2) 547.67(20)</td>
</tr>
<tr>
<td>60</td>
<td>147.02(5)</td>
<td>8.15(2)</td>
<td>6.6753(9) 12.167(3) 542.16(22)</td>
</tr>
<tr>
<td>70</td>
<td>144.13(4)</td>
<td>9.5(2)</td>
<td>6.662(1) 12.137(3) 538.67(24)</td>
</tr>
</tbody>
</table>
Figure S5. Example of a Rietveld refinement used in the determination of the equation of state for holmium pyrogermanate. The data were collected under an applied load of 50 tonnes. The tick marks represent the three phases used in the refinement. Upper: diamond, middle: NaCl, lower: Ho2Ge2O7 pyrogermanate.

3.2 Pyrochlore

An example refinement from the equation of state determination is shown in Figure S6 and the tabulated results in Table S2. The refinement used the following parameters:

- 22 variables.
- 3510 datapoints.
- wRp = 6.21%, Rp = 5.76%.
- 3 phases: Ho₂Ge₂O₇ (25 wt%), MgO (28 wt%), Al₂O₃ (47 wt%)
- Background function: shifted Chebyshev polynomial with 12 terms.
- Peak profile function: back-to-back exponentials convolved with pseudo-Voigt function (GSAS TOF profile 3). 3 refined terms for each phase (constrained to be equal).

Table S2. Refined parameters from the determination of the equation of state for the holmium germanate pyrochlore.

<table>
<thead>
<tr>
<th>Load (tonnes)</th>
<th>V (Å³)</th>
<th>Pressure (GPa)</th>
<th>Ho₂Ge₂O₇ (pyrochlore)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgO</td>
<td>a (Å)</td>
<td>V (Å³)</td>
</tr>
<tr>
<td>6</td>
<td>74.62(1)</td>
<td>0.18(2)</td>
<td>9.8971(9)</td>
</tr>
<tr>
<td>10</td>
<td>74.608(5)</td>
<td>0.210(5)</td>
<td>9.8968(8)</td>
</tr>
<tr>
<td>15</td>
<td>74.539(5)</td>
<td>0.360(2)</td>
<td>9.8948(7)</td>
</tr>
<tr>
<td>20</td>
<td>74.496(5)</td>
<td>0.450(1)</td>
<td>9.8932(8)</td>
</tr>
<tr>
<td>30</td>
<td>74.09(1)</td>
<td>1.337(8)</td>
<td>9.880(1)</td>
</tr>
<tr>
<td>40</td>
<td>73.41(1)</td>
<td>2.897(5)</td>
<td>9.8580(9)</td>
</tr>
<tr>
<td>45</td>
<td>73.07(1)</td>
<td>3.707(3)</td>
<td>9.8462(9)</td>
</tr>
</tbody>
</table>
Figure S6. Example of a Rietveld refinement used in the determination of the equation of state for the holmium germanate pyrochlore. The data were collected under an applied load of 50 tonnes. The tick marks represent the three phases used in the refinement. Upper: Al₂O₃, middle: MgO, lower: Ho₂Ge₂O₇ pyrochlore.