Tilting of semi-rigid GaF$_6$ octahedra in GaF$_3$ at high pressures

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The VF$_3$-type compound GaF$_3$ has been studied by high-pressure angle-dispersive X-ray diffraction in the pressure range from 0.0001 to 10 GPa. The compression mechanism was found to be highly anisotropic. The $c$-axis shows little pressure dependence ($\approx 0.4\%$), but exhibits negative linear compressibility up to $\approx 3$ GPa where it achieves its maximum length. In contrast, the length of the $a$-axis is reduced by $\approx 8.8\%$ at the highest measured pressure and an anomalous reduction in the linear compressibility is observed at 4 GPa. The zero pressure bulk modulus $B_0$ was determined to $B_0 = 28(1)$ GPa. The compression mechanism of GaF$_3$ is discussed in terms of deformation of an 8/3\overline{c} sphere-packing model. The volume reduction of GaF$_3$ is mainly achieved through coupled rotations of the GaF$_6$ octahedra within the entire measured pressure range, which reduces the volume of the cubooctahedral voids. In addition, the volume of the GaF$_6$ octahedra also decreases for $p \gtrsim 4.0$ GPa, but remains constant above this pressure. The volume reduction of the GaF$_6$ octahedra is accompanied by an increasing octahedral strain. Iso-surfaces of the Precrystal electron density are used for visualization of the cubooctahedral voids at different pressures. © 2017 International Centre for Diffraction Data. [doi:10.1017/S0885715616000701]

Key words: high-pressure, compression mechanism, void space

I. INTRODUCTION

Many metal triflourides, MF$_3$ including GaF$_3$, crystallize in the VF$_3$-type structure (Leblanc et al., 1985; Roos and Meyer, 2001). The VF$_3$ structure is composed of corner sharing MF$_6$ octahedra and therefore is structurally related to perovskite-type compounds AMX$_3$ as well as to the ReO$_3$ structure (Meisel, 1932). The non-distorted perovskite-type compounds are cubic with space group $Pm\overline{3}m$, while the VF$_3$ structure, which is derived from the ReO$_3$ structure by coupled rotations of the MF$_6$ octahedra around one of the cubic body diagonals, is rhombohedral with space group $R\overline{3}c$, which is a subgroup of $Pm\overline{3}m$. Structural changes of VF$_3$-type compounds are conveniently described as a rhombohedral deformation of a sphere packing of type 8/3\overline{c}2 (Sowa and Ahsbahs, 1998). The spheres of the 8/3\overline{c}2 sphere packing form octahedral and cuboctahedral voids, and each sphere has eight nearest-neighbour contacts and the smallest mesh has three edges (Fischer, 1973). The volume of the octahedral voids remains constant during a rhombohedral deformation of the 8/3\overline{c}2 sphere packing while the volume of the cuboctahedral voids is diminished. The anions of the VF$_3$-type compounds are in this model considered as hard spheres and the trivalent cations are located in the octahedral voids. The A-cation site is vacant in the VF$_3$-type structure and the simplest conceivable compression mechanism of compounds belonging to this structure type is a coupled rotation of the MF$_6$ octahedra around the $c$-axis (hexagonal setting), which will shorten the length of the $a$-axis and diminish the volume of the cuboctahedral voids while leaving the length of the $c$-axis unchanged. The linear compressibility of the $a$-axis is expected to be high as the restoring force is because of the bending of the M–F–M bonds, and a 30° rotation around one of the body diagonals of the $Pm\overline{3}m$ structure leads to the hexagonal close packing of the framework atoms X. The $\angle$F–M–F bond angle decreases from 180° in the cubic $Pm\overline{3}m$ structure to 131.8° when hexagonal close packing of the F atoms is achieved.

Several studies of the compression mechanism of VF$_3$-type compounds have been performed using both X-ray and neutron diffraction techniques. TiF$_3$ and FeF$_3$ were studied by high-pressure X-ray diffraction and both compounds were found to exhibit pressure-induced octahedral strain at elevated pressures. The compression mechanism was found to be anisotropic as the volume reduction was achieved through shortening of the hexagonal $a$ lattice parameter, while $c$-lattice parameter was found to exhibit a small elongation for increasing pressures (Sowa and Ahsbahs, 1998). In addition, CrF$_3$ and FeF$_3$ have been studied by time-of-flight neutron powder diffraction and these studies showed that the $\angle$Cr–F–Cr bond angle was reduced from 144.8(7)° to 133.9(4)° at $p_{\text{max}} = 8.56$ GPa, while the corresponding $\angle$Fe–F–Fe bond angle was reduced from 152.5(2)° to 134.8(3)° at $p_{\text{max}} = 8.28$ GPa and both compounds were observed to develop pressure-induced octahedral strain (Jørgensen et al., 2004, Jørgensen and Smith, 2006). The aim of the present experiment was to obtain detailed structural information on GaF$_3$ at elevated pressures.

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II. EXPERIMENTAL

High-pressure X-ray diffractograms were measured on a powdered GaF$_3$ sample (Aldrich) loaded in a diamond anvil cell with methanol/ethanol (4:1) mixture as a pressure-transmitting medium. The sample was loaded into a hole of 200 μm in diameter drilled in a stainless steel gasket pre-\textit{deed} to 70 μm. The measurements were performed at the Swiss-Norwegian Beam Lines (BM1A) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) using a wavelength of 0.69775 Å and MAR345 image plate detector. The wavelength, sample-to-detector distance (250 mm) and parameters of the detector were calibrated using NIST standard LaB$_6$. The beam was slit collimated to 100 × 100 μm$^2$. Pressure was determined on a ruby crystal with precision (Forman et al., 1972; Mao et al., 1986). The recorded powder patterns were first integrated in the FIT2D software and then analysed by the Rietveld method using a wavelength of 0.69775 Å and MAR345 image plate detector. The wavelength, sample-to-detector distance (250 mm) and parameters of the detector were calibrated using NIST standard LaB$_6$. The beam was slit collimated to 100 × 100 μm$^2$. Pressure was determined on a ruby crystal with precision (Forman et al., 1972; Mao et al., 1986). The recorded powder patterns were first integrated in the FIT2D software and then analysed by the Rietveld method using the FullProf program suite (Rodríguez-Carvajal, 1993). CrystalExplorer (Version 3.1) was used for illustrating void spaces (Wolff et al., 2012).

III. RESULTS AND DISCUSSION

Powder diffraction profiles of GaF$_3$ were recorded in the pressure range from 0.0001 to 10 GPa and inspection of the

<table>
<thead>
<tr>
<th>$p$ (GPa)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$x$</th>
<th>$R_{Bragg}$ (%)</th>
<th>$R_{R}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>4.9818(3)</td>
<td>13.016(1)</td>
<td>0.5995(7)</td>
<td>4.34</td>
<td>3.50</td>
</tr>
<tr>
<td>1.0</td>
<td>4.9244(4)</td>
<td>13.018(1)</td>
<td>0.6069(8)</td>
<td>4.62</td>
<td>3.18</td>
</tr>
<tr>
<td>2.0</td>
<td>4.8553(4)</td>
<td>13.030(1)</td>
<td>0.6151(8)</td>
<td>4.39</td>
<td>2.98</td>
</tr>
<tr>
<td>3.0</td>
<td>4.7851(5)</td>
<td>13.039(1)</td>
<td>0.6181(9)</td>
<td>7.13</td>
<td>4.81</td>
</tr>
<tr>
<td>4.0</td>
<td>4.7077(4)</td>
<td>13.032(1)</td>
<td>0.6321(1)</td>
<td>5.22</td>
<td>4.02</td>
</tr>
<tr>
<td>5.0</td>
<td>4.6736(4)</td>
<td>13.015(1)</td>
<td>0.6350(9)</td>
<td>4.01</td>
<td>3.64</td>
</tr>
<tr>
<td>6.0</td>
<td>4.6426(4)</td>
<td>12.999(1)</td>
<td>0.6379(9)</td>
<td>4.08</td>
<td>3.99</td>
</tr>
<tr>
<td>7.0</td>
<td>4.6186(4)</td>
<td>12.997(1)</td>
<td>0.6430(8)</td>
<td>3.35</td>
<td>2.80</td>
</tr>
<tr>
<td>8.0</td>
<td>4.5890(6)</td>
<td>12.988(2)</td>
<td>0.6485(9)</td>
<td>4.02</td>
<td>2.95</td>
</tr>
<tr>
<td>9.0</td>
<td>4.5670(8)</td>
<td>12.977(2)</td>
<td>0.651(1)</td>
<td>...</td>
<td>3.41</td>
</tr>
<tr>
<td>10.0</td>
<td>4.5435(8)</td>
<td>12.958(3)</td>
<td>0.655(1)</td>
<td>5.45</td>
<td>3.68</td>
</tr>
</tbody>
</table>

Space group: $R\bar{3}$ $c$, Ga: 6b (0 0 0), F: 18e ($\overline{1}$).

peak profiles gave no indication of any change of symmetry. Rietveld refinements of the measured powder diffraction profiles were therefore performed in space group $R\bar{3}$ $c$. Small Bragg peaks originating from a minor impurity of GaF$_3$·3H$_2$O were visible in powder patterns recorded for $p \leq 3$ GPa. The GaF$_3$·3H$_2$O phase was included in the Rietveld refinements for $p \leq 3$ GPa using structural parameters from the isostructural fluoro-hydrate CrF$_3$·3H$_2$O (Herbstein et al., 1985). The refined structural parameters of GaF$_3$ are given in Table I and Figure 1 shows, as a representative example, the measured and calculated X-ray powder diffraction profiles of GaF$_3$ at 10 GPa. The pressure dependence of the lattice parameters $a$ and $c$ (hexagonal setting) is shown in Figure 2. The $a$-axis decreases monotonically with the pressure and it is reduced by 8.8% at the highest measured pressure of 10 GPa and a change in the linear compressibility is observed at $\approx$4 GPa. The pressure dependence of the $c$-axis is much smaller and non-monotonic as it exhibits a maximum at 3 GPa (0.17% increase), while the overall reduction is 0.4% at 10 GPa. The insert of Figure 2 shows the $\sqrt{3/3} \cdot c/a$ ratio vs. pressure. This ratio is equal to 1.633 at $\approx$7.9 GPa corresponding to hexagonal close packing of the fluorine atoms. The volume of the unit cell is plotted as a function of pressure in Figure 3 and a change in the compressibility is again observed at $\approx$4 GPa where the compressibility is seen to decrease. The unit-cell volume is reduced by 10.6% at $4 \leq p \leq 4$ GPa and the reduction increases to 17.2% at 10 GPa. The data measured for $4 \leq p \leq 4$ GPa were used for the determination of the bulk modulus $B_0$ of GaF$_3$ by use of the third-order Birch–Murnaghan equation of state:

\[
P = \frac{3}{2} B_0 (x^{-7/3} - x^{-5/3}) \left[1 - \frac{3}{4} (4 - B'_0)(x^{2/3} - 1)\right],
\]

where $x$ denotes the volume ratio $V/V_0$ (with $V_0$ being the volume at zero pressure) while $B_0$ and $B'_0$ are the isothermal bulk modulus at ambient pressure and its pressure derivative, respectively. The least-squares fit to the measured data yielded the following value for the bulk modulus: $B_0 = 28(1)$ GPa with $B'_0$ and fixed at the values of 4 and $V_0 = 282(2)$ Å$^3$.

Figure 1. (Color online) Observed (red dots) and calculated (black curve) X-ray powder diffraction profiles of GaF$_3$ at 10 GPa. Green vertical bars mark the positions of the Bragg reflections and the lower blue curve represents the difference between the observed and calculated intensities.
The simplest description of the compression mechanism of VF₃-type compounds is in terms of deformation of an $8/3\sqrt{3}c$ sphere-packing model in space group $R\bar{3}c$ as mentioned above and the $x$-coordinate of the spheres (F atoms) is in this model determined by $cla$ ratio and given by Sowa and Ahsbahs (1998):

$$x = \frac{1}{2} \pm \left[ \frac{c^3}{72a^2} - \left(\frac{1}{12}\right) \right]^{1/2}.$$  \hspace{1cm} (2)

Figure 4 shows the $c/\alpha$ ratio plotted as function of the refined fluorine $x$-coordinates. The deformation of the $8/3\sqrt{3}c$ sphere-packing model gives a reasonable description of the compression mechanism of GaF₃ as the observed linear compressibility for GaF₃ show an increasing deviation from the sphere packing model at elevated pressures and the non-monotonous pressure dependence of the length of the $c$-axis is also at variance with the predictions of the $8/3\sqrt{3}c$ sphere-packing model, which predicts a constant length of this axis during compression.

The pressure-induced structural changes of the GaF₆ octahedra are depicted in Figures 5 and 6. The Ga–F bond length and the two independent F–F distances $d_1$ and $d_2$ within the GaF₆ octahedra are plotted as function of pressure in Figure 5, which shows that the Ga–F bond length is reduced by 0.8% at 10 GPa, while the F–F distances $d_1$ and $d_2$ decrease monotonically by 2.1 and 1.0%, respectively, up to $\approx 4$ GPa and become constant above this pressure. Figure 6 shows the volume of the GaF₆ octahedra and the octahedral strain for GaF₃.
from 145.01(5)° to 135.00(8)° within the pressure range [52x465]of the GaF6 octahedra along the corresponding almost hexagonally close packed at this pressure. The corre-
of the total volume reduction at 4 GPa and the increasing volume of the GaF6 octahedra is reduced by 4.6% at the GaF6 octahedra also explains the fact that the GaF3 is achieved through reduction of the volume of the [52x373]it increases from 19.0(1)° at ambient pressure to 24.5(2)° at elevated pressures. Compression of GaF3 is therefore almost to 28.2(2)° at 10 GPa, showing that the cubooctahedral voids in this pressure range where entirely achieved through reduction of the volume of the [52x327]compression of GaF3 shows that they become almost rigid polyhedra [52x505]at pressures higher than [52x522]initially also increases and saturates at a constant value for pressures higher than ≈3 GPa. The initial volume reduction of 4.6% of the GaF6 octahedra therefore accounts for ≈43% of the total volume reduction at 4 GPa and the increasing degree of distortion reflects an increasing elongation of the GaF6 octahedra along the c-axis ($d_1 < d_2$). The elongation of the GaF6 octahedra also explains the fact that the $\sqrt{3/3}$ ratio exceeds 1.633 for $p \geq 7.9$ GPa as shown in the insert of Figure 2. The above-mentioned coupled rotation angle $\omega$ of the GaF6 octahedra around the c-axis is calculated from the refined fluorine $x$-coordinates. A calculation of $\omega$ shows that it increases from 19.01(1)° at ambient pressure to 24.5(2)° at 4 GPa, and it is therefore concluded that compression of GaF3 is achieved through reduction of the volume of the GaF6 octahedra as well as through reduction of the volume of the cuboctahedral voids for $p \leq 4$ GPa. The observed constant values of volume and strain of the GaF6 octahedra for $p \geq 4$ GPa show that they become almost rigid polyhedra at elevated pressures. Compression of GaF3 is therefore almost entirely achieved through reduction of the volume of the cuboctahedral voids in this pressure range where $\omega$ increases to 28.2(2)° at 10 GPa, showing that the fluorine atoms are almost hexagonally close packed at this pressure. The corre-
sponding $\angle$Ga–F–Ga bond angle was found to decrease from 145.01(5)° to 135.00(8)° within the pressure range from 0.0001 to 10 GPa and thereby approaching the value of 131.8° predicted by the 8/3c/2 sphere-packing model in the limit of hexagonally close packed spheres.

The reduction of the volume of the cuboctahedral voids is visualized in Figure 7, which shows the crystal structures of GaF3 and the cuboctahedral voids at ambient pressure, 5 and 10 GPa. The cuboctahedral voids are visualized as isosurfaces of the procrystal electron density (Turner et al., 2011). The three isosurfaces are drawn for isovalues of 0.005 $eÅ^3$ and cuboctahedral voids are seen to shrink for increasing pressures as predicted by the 8/3c/2 sphere-packing model. The volume of the cuboctahedral voids is reduced by 79% at 5 GPa and almost absent (99% reduction) at 10 GPa consistent with the proximity to close packing of the F$^-$ ions at this pressure as described above.

A comparison of the high-pressure behaviour TiF3, CrF3, FeF3, and GaF3 shows that their compression mechanisms are very similar although with minor differences. The $c$-axis of all four compounds exhibits negative linear compressibility at lower pressures and the octahedral strain $\varepsilon$ increases at elevated pressures for all four compounds. The $c$-axis of TiF3 is elongated by 2.9% between 0.0001 and 5 GPa (Sowa and Ahsbahs, 1998), which is substantially larger than the corre-
spending values of 0.17% observed for GaF3 and CrF3 (Jørgensen et al., 2004). In the case of FeF3 intermediate elongations of 0.77 and 1.1% of the $c$-axis have been observed (Sowa and Ahsbahs, 1998; Jørgensen and Smith, 2006). The octahedral strain $\varepsilon$ of GaF3 saturates at ≈0.009 for $p \geq 3$ GPa, which is comparable with the corresponding $\varepsilon$ values of 0.005 and 0.008 for CrF3 and FeF3, respectively (Jørgensen et al., 2004, Jørgensen and Smith, 2006). In addition, analysis of the results of Sowa and Ahsbahs (1998) for TiF3 and FeF3 shows that the octahedral strain $\varepsilon$ increases linearly up to about 3 GPa and saturates at values of 0.014 and 0.0063 for TiF3 and FeF3, respectively. However, in contrast to the high-pressure neutron diffraction studies of CrF3 and FeF3 (Jørgensen et al., 2004, Jørgensen and Smith, 2006), no structural refinement was done in this study (Sowa and Ahsbahs, 1998), which was based on the assumption that the metal–fluorine bond length is independent of the pressure. Most interestingly, the observed change in the compressibility of GaF3 at ≈4 GPa as well as the initial reduction of volume of the GaF6 octahedra seems to be unique to this compound. The change in compressibility and the initial reduction of the volume of the GaF6 octahedra is mainly because of changes in the
Ga–F bond length and $d_1$ F–F distance. The Ga–F bond length and $d_1$ F–F distance decreases up to about 4 GPa and becomes constant above this pressure and similar behaviour is not observed in the earlier high-pressure studies of CrF$_3$ and FeF$_3$ (Jørgensen et al., 2004, Jørgensen and Smith, 2006).

IV. CONCLUSION

The compression mechanism of GaF$_3$ was found to be highly anisotropic with the lengths of $a$- and $c$-axes being reduced by 8.8 and 0.4%, respectively, at the highest measured pressure of 10 GPa. The initial compression up to about 4 GPa is achieved through coupled rotations of the GaF$_6$ octahedra around the $c$-axis, which is accompanied by volume reduction and distortion of the GaF$_6$ octahedra, which become rigid polyhedral for pressures higher than 4 GPa. Compression at higher pressures is entirely achieved through the coupled rotation of the GaF$_6$ octahedra which reduces the volume of the cubooctahedral voids. In addition, our work shows the usefulness of isosurfaces of the procrystal electron density for illustrating changes in void space in crystals at elevated pressures.

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