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ABSTRACT

The VF3-type compound GaF3 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 (~0.4%), but exhibits negative linear compressibility up to ~3 GPa where it achieves its maximum length. In contrast, the length of the a-axis is reduced by ~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 B0 was determined to B0 = 28(1) GPa. The compression mechanism of GaF3 is discussed in terms of deformation of an 8/3/c2 sphere-packing model. The volume reduction of GaF3 is mainly achieved through coupled rotations of the GaF6 octahedra within the entire measured pressure range, which reduces the volume of the cubooctahedral voids. In addition, the volume of the GaF6 octahedra also decreases for p ≤ 4.0 GPa, but remains constant ab...

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**TECHNICAL ARTICLE**

**Tilting of semi-rigid GaF₆ octahedra in GaF₃ at high pressures**

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The VF₃-type compound GaF₃ 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 (≈0.4%), but exhibits negative linear compressibility up to ≈3 GPa where it achieves its maximum length. In contrast, the length of the a-axis is reduced by ≈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 B₀ was determined to B₀ = 28(1) GPa. The compression mechanism of GaF₃ is discussed in terms of deformation of an 8/3/c2 sphere-packing model. The volume reduction of GaF₃ is mainly achieved through coupled rotations of the GaF₆ octahedra within the entire measured pressure range, which reduces the volume of the cubooctahedral voids. In addition, the volume of the GaF₆ octahedra also decreases for p ≥ 4.0 GPa, but remains constant above this pressure. The volume reduction of the GaF₆ octahedra is accompanied by an increasing octahedral strain. Isosurfaces of the procrystal 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 trifluorides, MF₃ including GaF₃, crystallize in the VF₃-type structure (Leblanc et al., 1985; Roos and Meyer, 2001). The VF₃ structure is composed of corner-sharing MF₆ octahedra and therefore is structurally related to perovskite-type compounds AM₃ as well as to the ReO₃ structure (Meisel, 1932). The non-distorted perovskite-type compounds are cubic with space group Pm″m, while the VF₃ structure, which is derived from the ReO₃ structure by coupled rotations of the MF₆ octahedra around one of the cubic body diagonals, is rhombohedral with space group R3c, which is a subgroup of Pm″m. Structural changes of VF₃-type compounds are conveniently described as a rhombohedral deformation of a sphere packing of type 8/3/c2 (Sowa and Ahsbahs, 1998). The spheres of the 8/3/c2 sphere packing form octahedral and cubooctahedral 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/c2 sphere packing while the volume of the cubooctahedral voids is diminished. The anions of the VF₃-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 VF₃-type structure and the simplest conceivable compression mechanism of compounds belonging to this structure type is a coupled rotation of the MF₆ octahedra around the c-axis (hexagonal setting), which will shorten the length of the a-axis and diminish the volume of the cubooctahedral 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″m structure leads to the hexagonal close packing of the framework atoms X. The ζM–F–M bond angle decreases from 180° in the cubic Pm″m structure to 131.8° when hexagonal close packing of the F atoms is achieved.

Several studies of the compression mechanism of VF₃-type compounds have been performed using both X-ray and neutron diffraction techniques. TiF₃ and FeF₃ 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, CrF₃ and FeF₃ have been studied by time-of-flight neutron powder diffraction and these studies showed that the ζCr–F–Cr bond angle was reduced from 144.80(7)° to 133.9(4)° at p = 8.56 GPa, while the corresponding ζFe–F–Fe bond angle was reduced from 152.5(2)° to 134.8(3)° at p = 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 GaF₃ at elevated pressures.

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II. EXPERIMENTAL

High-pressure X-ray diffractograms were measured on a powdered GaF₃ 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 preindented 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 LaB₆. The beam was slit collimated to 100 × 100 µm². 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 GaF₃ were recorded in the pressure range from 0.0001 to 10 GPa and inspection of the peak profiles gave no indication of any change of symmetry. Rietveld refinements of the measured powder diffraction profiles were therefore performed in space group R3c. Small Bragg peaks originating from a minor impurity of GaF₃·3H₂O were visible in powder patterns recorded for p ≤ 3 GPa. The GaF₃·3H₂O phase was included in the Rietveld refinements for p ≤ 3 GPa using structural parameters of the isostructural fluoro-hydrate CrF₃·3H₂O (Herbstein et al., 1985). The refined structural parameters of GaF₃ are given in Table I and Figure 1 shows, as a representative example, the measured and calculated X-ray powder diffraction profiles of GaF₃ 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 ±4 GPa. The pressure dependence of the c-axis is much smaller and non-monotonous 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 √3/a ratio vs. pressure. This ratio is equal to 1.633 at ±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 ±4 GPa where the compressibility is seen to decrease. The unit-cell volume is reduced by 10.6% at 4 GPa and the reduction increases to 17.2% at 10 GPa. The data measured for p ≤ 4 GPa were used for the determination of the bulk modulus B₀ of GaF₃ 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/V₀ (with V₀ being the volume at zero pressure) while B₀ and B₀' 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: B₀ = 28(1) GPa with B₀' fixed at the values of 4 and V₀ = 282(2) Å³.

Table I. Refined structural parameters for GaF₃.

<table>
<thead>
<tr>
<th>p (GPa)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>x</th>
<th>R_Bragg (%)</th>
<th>R_Riet (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>4.9818(3)</td>
<td>13.0161(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>13.0181(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>13.0301(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>13.0391(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>13.0321(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>13.0151(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>12.9991(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>12.9971(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>12.9882(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>12.9772(2)</td>
<td>0.6511(1)</td>
<td>...4.72</td>
<td>3.41</td>
</tr>
<tr>
<td>10.0</td>
<td>4.5435(8)</td>
<td>12.9583(3)</td>
<td>0.6551(1)</td>
<td>5.45</td>
<td>3.68</td>
</tr>
</tbody>
</table>

Space group: R3c #167, Ga: 6b (0 0 0), F: 18e (0 1/3).

Figure 1. (Color online) Observed (red dots) and calculated (black curve) X-ray powder diffraction profiles of GaF₃ 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 8/3c² sphere-packing model in space group R̅3c 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):

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

Figure 4 shows the c/a ratio plotted as function of the refined fluorine x-coordinates. The deformation of the 8/3c² sphere-packing model gives a reasonable description of the compression mechanism of GaF₃ as the observed linear compressibility the a-axis is substantially larger than that of the c-axis. However, minor but significant deviations from the sphere-packing model are observed and the refined cla and x-values 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 8/3c² 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 d₁ and d₂ 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 d₁ and d₂ decrease monotonically by 2.1 and 1.0%, respectively, up to ≈4 GPa and become constant above this pressure. Figure 6 shows the volume of the GaF₆ octahedra and the octahedral strain for GaF₃.
The volume of the GaF₆ octahedra is reduced by 4.6% at ≈4 GPa and stays constant above this pressure. The octahedral strain ε 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 nearly 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 (d₁ < d₂). The elongation of the GaF₆ octahedra also explains the fact that the ratio of the total volume reduction at 4 GPa and the increasing degree of distortion for the GaF₆ octahedra along the c-axis exceeds 1.633 for p ≥ 7.9 GPa as shown in the insert of Figure 2. The above-mentioned coupled rotation angle ω of the GaF₆ octahedra around the c-axis is calculated from the refined fluorne coordinates. A calculation of ω 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 ≤ 4 GPa. The observed constant values of volume and strain of the GaF₆ octahedra for p ≥ 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 ω increases to 28.2(2)° at 10 GPa, showing that the fluoride atoms are almost hexagonally close packed at this pressure. The corresponding θGa–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 8/3c2 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 8/3c2 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 ε 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 corresponding 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 ε of GaF₃ saturates at ≈0.009 for p ≥ 3 GPa, which is comparable with the corresponding ε 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 ε 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 seems to be unique to this compound. The change in compressibility and the initial reduction of the volume of the GaF₆ octahedra seems to be unique to this compound.
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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