The Phase Diagram of K₃FeF₆ to 35 kbar and 600 °C

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High Pressure Phase Diagram, D. T. A.

The effect of pressure on the tetragonal/cubic phase transition in K₃FeF₆ was studied to 35 kbar. A new phase which also occurs in K₃TiF₆, exists over a small temperature region at low pressures. A strong possibility exists that the K₃FeF₆ tetragonal phase is isomorphous with the corresponding phase found for the K₃XF₆ (X = Ln, Y) compounds.

Introduction

A wide range of polymorphic behaviour is known to occur for the stoichiometric compounds A₃MF₆ that exist in the AF–BF₃ system (A = Ti, Na, K, Rb, Cs, Ag, NH₄ and M = Y, Ti, V, Al, Fe, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb). X-ray diffraction and infrared studies of the compounds A₃FeF₆ indicated that the phase stable at ambient conditions is tetragonal with at least the symmetry of space group I₄, except for A = Na, which is monoclinic and A = Ti and NH₄ which are cubic. At higher temperatures the stable phase for all compounds is cubic with space group Fm3m.

The phase behaviour for the K₃XF₆ group of substances (X = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Y) is more complex. Three solid-solid phase transitions occur with increasing temperature throughout the series. The room temperature phase is monoclinic with possible space groups P2₁/n or P2₂₁/n with a cryolite-based structure. This phase transforms on heating to another monoclinic phase with space group P2₁/n, which has a structure related to that of perovskite. At still higher temperatures two more phases appear which are tetragonal, space group I₄/mmm and cubic, space group Fm3m respectively. Both high temperature phases appear to have distorted cryolite structures. The effect of pressure on the transition temperature of some of the above phase transitions in K₃SmF₆ and K₃YF₆ to 35 kbar has been reported.

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The present study was undertaken to investigate the effect of pressure on the tetragonal/cubic phase transition in K₃FeF₆.

Experimental

K₃FeF₆ was prepared from KF and FeF₃ which were obtained from Koch-Light Laboratories. The stated purity of FeF₃ was 98%+. The stoichiometric mixture was sealed in a silver capsule and heated at 700 °C for 100 hours. X-ray diffraction showed that the product was single phase.

Pressures of up to 35 kbar were generated in a piston-cylinder apparatus. The phase transformations were studied by means of differential thermal analysis (D. T. A.) using chromel-alumel thermocouples. The samples were contained in monel capsules and post-mortem X-ray analysis showed no evidence of contamination or decomposition. Heating/cooling rates varied between 0.1–1.5 °C/s. The phase boundaries were taken to be the mean of the transition temperatures obtained on heating and cooling and are based on three consistent runs. The final boundaries are believed to be better than ±2 degrees and ±0.5 kbar. The detailed experimental procedure has been described elsewhere.

Results and Discussion

The phase diagram of K₃FeF₆ is shown in Fig. 1. The D. T. A. and D. S. C. (differential scanning calorimeter) atmospheric pressure results indicated that the room temperature phase did not transform directly to the cubic high temperature phase as reported in the literature. A new phase K₃FeF₆ II, which is less dense than the tetragonal phase, but more dense than the cubic phase, exists over a short temperature range between the tetragonal and cubic phases [Fig. 2(i)]. The present atmospheric pressure transition temperatures for the K₃FeF₆
The III/II and II/I transitions are 177 °C and 227 °C, respectively. This is somewhat higher than the single value of 140 ± 10 °C reported in the literature. No transition was observed at 140 °C in the present study. Pressure stabilizes phase III with respect to phase II, as the III/II phase boundary rises steeply with pressure to meet the II/I phase boundary in the I/III/II triple point where the stability field of K₃FeF₆ II is terminated. The triple point was taken to be at 2.3 kbar, 251 °C. This coordinate may be somewhat uncertain because of the usual difficulty in obtaining accurate values for the sliding friction at such low pressures. At pressures above the triple point phase III transforms directly to phase I. The D. T. A. signals of this transition were broader than those of the other two transitions [Fig. 2(ii)], but could be followed to 34 kbar, 589.8 °C. The phase relations of K₃FeF₆ are given in Table I.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Least-squares fit</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₃FeF₆ III/I</td>
<td>t(C) = 251.0 + 12.0(P - 2.34) - 442(P - 2.34)^2</td>
<td>2.0 °C</td>
</tr>
<tr>
<td>K₃FeF₆ III/II/I</td>
<td>Pressure</td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td>[kbar]</td>
<td>[°C]</td>
</tr>
<tr>
<td>K₃FeF₆ III/II/I</td>
<td>2.3</td>
<td>251</td>
</tr>
</tbody>
</table>

The heat effects associated with the III/II and II/I transitions at atmospheric pressure are 5.0 and 4.1 J/mole K, respectively, which, together with the mean slopes of 32.2 and 10.4 °C/kbar of the respective phase boundaries and the Clapeyron relation, yield

\[ \Delta V_{III/II} \approx 1.6 \text{ cm}^3/\text{mole} \]

and

\[ \Delta V_{II/I} \approx 0.4 \text{ cm}^3/\text{mole}. \]

No accurate calculation of the volume changes at the triple point could be made due to the uncertainty in curvature and slopes of the phase boundaries caused by the uncertainty in the co-ordinates of the triple point. It is known, however, from additive relationships at the triple point that, \( \Delta V_{III/II, \text{ triple point}} \) is the sum of \( \Delta V_{II/I, \text{ at the triple point}} \) and \( \Delta V_{II/III, \text{ at the triple point}} \), and should therefore be about 1 to 2 cm³/mole. This corresponds to a volume change of \( \sim 2\% \) if \( a_{\text{tetra}} = 6.07 \text{ Å} \) and \( c_{\text{tetra}} = 8.66 \text{ Å} \).
if it is assumed that $Z = 2$, as is the case in tetragonal $K_3AXF_6$ ($X = \text{Ln, Y}$). The corresponding value that can be derived from crystallographic data in the literature\(^1\) is $\sim 3\%$, but this includes the thermal expansion between 25 °C and 300 °C. The true value of $AV_{\text{HIV}}$ will therefore be lower than 3%, which is in good agreement with the present value.

It is known that related compounds, e.g. $Na_3AlF_6$, $Na_3FeF_6$, $Na_3VF_6$ and $Na_3TiF_6$ tend to have related P-T phase diagrams\(^1\)\(^2\). It is therefore highly probable that the tetragonal phase in $K_3FeF_6$ has the same structure and space group, i.e. $I4/mmm$, as that of the tetragonal phase in $K_3AXF_6$ ($X = \text{Ln, Y}$). If this is the case, it is also possible to predict that two monoclinic phases similar to $K_3SmF_6$ and $K_3YF_6$ III and IV\(^7\) exist at lower temperatures for $K_3FeF_6$.

The nature of the $K_3FeF_6$ II phase is not known, but it also appears to exist in $K_3TiF_6$, as we

obtained D. T. A. signals at 151 °C and 200 °C at atmospheric pressure for the latter compound. It would not be surprising if a similar phase is found to exist in $K_3AlF_6$, $K_3VF_6$ and related compounds of some of the other transition metals. It should also be noted that this phase supposedly does not have an equivalent amongst the $K_3XF_6$ ($X = \text{Ln, Y}$) compounds where the tetragonal phase always disorders directly to the cubic high temperature phase. Further crystallographic studies of the above phase need to be done.

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