Growth by Hydrothermal Synthesis and Some Properties of Synthetic Cryolite Single Crystal*

By Kazutaka Kawamura**

The present study was made in the hope of preparing a large synthetic single crystal of cryolite. As a result of many attempts, the hydrothermal synthesis is proved to be most satisfactory. The cryolite crystal grown is as large as 2.0 × 1.5 × 0.8 mm and free from the OH radical.

The characterization of the synthetic cryolite is investigated by the differential scanning calorimeter and the Raman spectrometer.

The specific heat for the synthetic cryolite is expressed as a function of temperature:

\[ C_p = 183.9 + 141.9 \times 10^{-3} T. \]

The force constants of stretching, deformation and non-bonding for the synthetic single crystal of cryolite are \((3.63 \pm 0.025) \times 10^2\), \((0.41 \pm 0.013) \times 10^2\) and \((0.30 \pm 0.00) \times 10^2\) Nm\(^{-1}\), respectively.

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I. Introduction

The structure of molten electrolyte containing cryolite has been a subject of many investigations because of its industrial importance as the solvents for alumina in the electrolytic production of aluminium. Several chemical forms of fluoro complex anions in molten electrolyte in an equilibrium state have been suggested indirectly from the results of various experiments on E.M.F., density, surface tension, electrical conductivity, viscosity, and vapor pressure. It is generally accepted that the presence of these species, to some extent, is confirmed spectroscopically by comparing the reference spectra of a pure single crystal of cryolite with the spectra of the molten electrolyte.

The available single crystal of cryolite is only a natural one which contains usually a small amount of impurities such as iron oxide and silica, but not a synthetic one which is completely free from impurities. Few attempts, to my knowledge, have been made to prepare the single crystal of cryolite.

The only successful preparation of the synthetic single crystal of cryolite was carried out by Michel-Levy et al.\((1)\) who obtained a fine single crystal by the reaction between sodium fluorosilicate and aluminium oxide in the presence of water under a pressure of \(3.9 \times 10^2\) MPa at 773 K for 0.78 Ms. However, their method had the disadvantages that the obtained cryolite was very fine, i.e., \((2 \sim 3) \times 10 \mu m\) and was mixed with a topaz (\(Al_2SiO_4F_2\)) due to the following chemical reaction:

\[ 3Na_2SiF_6 + 4Al_2O_3 = 3Al_2SiO_4F_2 + 2Na_3AlF_6. \]

\[(1)\]

The present study has been carried out in order to prepare a large synthetic single crystal of cryolite which is isolated from the crystal of other composition such as topaz. Many attempts made, heretofore have proved the hydrothermal synthesis to be most satisfactory. Moreover, the fine powder of synthetic cryolite is used as a starting material in the present work, so that the obtained cryolite crystal is not mixed with the crystal of other composition in contrast with Levy's method as mentioned above.

In order to obtain some characteristics of the synthetic single crystal of cryolite, the thermal and spectroscopic (vibrational) behaviors are chosen and investigated by the differential scanning calorimeter and the Raman spectrometer, respectively.

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II. Experimental

1. Preparing method for synthetic single crystal of cryolite—hydrothermal synthesis

The very fine powder of synthetic cryolite has been obtained by many procedures such as HF–Al(OH)₃–Na₂CO₃, Al₂SO₄–NaF, hot press, and heat treatment methods (2). However, in the course of these experiments, it is found that a very small amount of cryolite dissolves in water. Such a solubility suggests that water might be a medium adequate for preparing the synthetic single crystal of cryolite. Thus, hydrothermal synthesis was applied to prepare the single crystal of cryolite. The hydrothermal synthesis was carried out in an autoclave, as shown in Fig. 1, which was made of Stellite (Cr(20 wt %)–W(15 wt %)–Ni(10 wt %)–Fe(3 wt %)–Mn(1.5 wt %)–Si(1.0 wt %)–Co(Bal.)). The lid of the autoclave was made of stainless steel (SUS 304) and the inner lining of the autoclave was a platinum sheet of 0.3 mm thickness.

2 g of the synthetic cryolite powder and 30 cm³ of distilled water were put in the autoclave. The pressure over 0.49 MPa was applied from the air or nitrogen cylinder. The autoclave was then heated at various temperatures for different times under varying pressures in order to find an optimum condition for the preparation of the single crystal of cryolite.

2. Specific heat of synthetic single crystal of cryolite

Specific heat measurement was carried out by the Perkin Elmer Model DSC-2 differential scanning calorimeter. Single crystal of cryolite was ground to powder and 9.6 mg of the pulverized cryolite was employed.

In this experiment, a sample of known specific heat such as synthetic sapphire was used as an external standard. The use of the external standard simplifies the operation and increases the accuracy obtainable.

3. Raman spectra of synthetic single crystal of cryolite

Raman spectrum measurement was made with a Shimazu Model R2D Raman spectrometer, coupled with a thermoelectrically cooled FW–130 photomultiplier tube and a photon counting system. Raman excitation was achieved with a Spectra-Physics Model 165 argon ion laser emitting about 400 mW at 488 nm.

III. Results and Discussion

1. Preparation of single crystal of cryolite

The results of hydrothermal synthesis are shown in Fig. 2. The temperature and heating time for growing the cryolite crystal are shown under varying pressures in this figure. It is obvious that the lowest temperature and the required heating time for the hydrothermal synthesis are 473 K and 0.72 Ms, respectively. The lowest temperature increases with decreasing heating time under a constant pressure, that is, the lowest temperature increases from 473 to 523 K with decreasing heating time from 0.72 to 0.18 Ms under the pressure of 1.96 MPa. It is also seen that the temperature increases with decreasing pressure for a constant heating time, that is, the temperature increases from 493 K to 523 K with the decrease of pressure from 1.96 MPa to 0.49
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Fig. 2 Growth of cryolite crystal in various experimental conditions.
- ○: Crystal growing
- △: Crystal growing microscopically
- ×: No crystal growing
Numerical values; Pressure expressed in MPa.

MPa for the heating period of 0.36 Ms.

The size of the grown crystal seems to be proportional to the temperature and the heating time; however, there appears a twin at temperature above 673 K.

Single crystals visible even to the naked eye are grown in the crystallization zone in which a water level is located. The crystals thus grown stick so weakly on an inside wall of the platinum lining that they could easily be removed. The fact suggests that the nucleation might take place at any position of the platinum lining surface instead of a preferred position of the lining surface as indicated clearly in the hydrothermal synthesis of magnetite by Hirano et al. (3)

While it might be expected that the fluoride crystal grown by hydrothermal synthesis would contain a small amount of the OH radical (4), the infrared spectrum of the synthetic cryolite does not show any evidence of the presence of the OH radical.

The most typical single crystal of cryolite obtained is shown in Photo. 1. The (100), (010), and (001) planes of this monoclinic single crystal of cryolite are determined by the Laue method and are shown in Photo. 2(a), 2(b), and 2(c), respectively.

2. Specific heat of synthetic cryolite

The experimental specific heat are summarized in Table 1 and are plotted against temperature in Fig. 3 together with the com-
Table 1 Experimental values of specific heat of synthetic cryolite.

<table>
<thead>
<tr>
<th>Temperature $T$ (K)</th>
<th>Specific heat $C_p$ (JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>356</td>
<td>233.53</td>
</tr>
<tr>
<td>380</td>
<td>239.45</td>
</tr>
<tr>
<td>405</td>
<td>243.34</td>
</tr>
<tr>
<td>430</td>
<td>243.90</td>
</tr>
<tr>
<td>455</td>
<td>248.81</td>
</tr>
<tr>
<td>480</td>
<td>251.67</td>
</tr>
<tr>
<td>505</td>
<td>255.22</td>
</tr>
<tr>
<td>530</td>
<td>260.08</td>
</tr>
<tr>
<td>555</td>
<td>261.15</td>
</tr>
<tr>
<td>580</td>
<td>267.17</td>
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<tr>
<td>605</td>
<td>270.60</td>
</tr>
<tr>
<td>630</td>
<td>272.68</td>
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<tr>
<td>655</td>
<td>276.25</td>
</tr>
<tr>
<td>680</td>
<td>281.34</td>
</tr>
<tr>
<td>705</td>
<td>285.48</td>
</tr>
<tr>
<td>730</td>
<td>287.14</td>
</tr>
</tbody>
</table>

Fig. 3 Specific heat of synthetic cryolite.

The equation best fitted for the observed values is calculated by using the least squares method and is expressed as follows:

$$C_p = 183.9 + 141.9 \times 10^{-3}T,$$  \hspace{1cm} (2)

where $C_p$ and $T$ are the specific heat in JK$^{-1}$mol$^{-1}$ and the temperature in K, respectively.

In a study of the specific heat of cryolite, it is of interest to compare the specific heat of cryolite with that of the stoichiometric summation of sodium fluoride and aluminium fluoride. The obtained specific heat of cryolite turns out to be greater than that of the stoichiometric summation. The difference increases with increase in temperature, varying from 0.1% at 356 K to 9% at 751 K.

3. Raman spectra for synthetic and natural cryolite

The Raman spectra of the isolated $\text{AB}_6$ ($\text{AlF}_3$) octahedron with $O_h$ point group symmetry are expected for only three of the six normal vibrations of such a species involved in the Raman effect\(^7\); $v_1$ ($A_{1g}$) symmetric stretching, $v_2$ ($E_g$) anti-symmetric stretching, and $v_5$ ($F_{2g}$) anti-symmetric deformation. The obtained band positions, band intensities and the assignments for both synthetic and natural single crystals of cryolite are listed in Table 2. The most significant band feature of the cryolite is a sharp and intense band at about $5.50 \times 10^4$ m$^{-1}$. In view of the rule that totally symmetric vibration gives rise to the strongest Raman line, it appears certain that the very strong line of about $5.50 \times 10^4$ m$^{-1}$ corresponds to...
Table 2 Assignment of the Raman spectrum for synthetic and natural single cryolite crystals (Point Group \(O_h\)).

<table>
<thead>
<tr>
<th>Wave number ((\times 10^4 \text{ m}^{-1}))</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic</td>
<td>Natural</td>
<td></td>
</tr>
<tr>
<td>3.82 ± 0.05</td>
<td>3.78 ± 0.05</td>
<td>v.w. (\nu_3)</td>
</tr>
<tr>
<td>4.87 ± 0.03</td>
<td>4.86 ± 0.10</td>
<td>v.w. (\nu_2)</td>
</tr>
<tr>
<td>5.51 ± 0.01</td>
<td>5.52 ± 0.01</td>
<td>s. (\nu_1)</td>
</tr>
<tr>
<td>10.35 ± 0.05</td>
<td>10.20 ± 0.10</td>
<td>w. —</td>
</tr>
</tbody>
</table>

v.w.: very weak
w.: weak
s.: strong

Table 3 Various force constants for synthetic and natural single cryolite crystals \((\times 10^2 \text{ Nm}^{-1})\).

<table>
<thead>
<tr>
<th>Force constant</th>
<th>Synthetic</th>
<th>Natural</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (Al–F)</td>
<td>3.63 ± 0.025</td>
<td>3.64 ± 0.013</td>
</tr>
<tr>
<td>H (F–Al–F)</td>
<td>0.41 ± 0.013</td>
<td>0.40 ± 0.013</td>
</tr>
<tr>
<td>F (F–F)</td>
<td>0.30 ± 0.00</td>
<td>0.30 ± 0.00</td>
</tr>
</tbody>
</table>

the totally symmetric Al–F stretching mode of \(\text{AlF}_6^{2-}\) group. Since one would expect \(\nu_2 > \nu_3\), the lines at about \(3.8 \times 10^4 \text{ m}^{-1}\) and about \(4.87 \times 10^4 \text{ m}^{-1}\) are assigned to \(\nu_5\) and \(\nu_2\) respectively \((7)(8)\).

Several force constants based on the Urey-Bradley force field \((9)\) are calculated from the obtained three Raman lines and are shown in Table 3. In this table, the force constants of K, H, and F correspond to the stretching of Al–F, the deformation of F–Al–F and the non-bonding of F–F, respectively. It seems reasonable that the value of K is about ten times larger than those of H and F. It should also be noted that there is no difference between the force constants for synthetic cryolite and those for natural cryolite within the experimental reliability.

### IV. Conclusion

The preparation based on hydrothermal synthesis is shown to give the large synthetic single crystal of cryolite. In this experiment, the single crystal is successfully grown from synthetic cryolite powder in the presence of water under pressures higher than 0.49 MPa at temperatures above 473 K for a period of 0.72 Ms. The required temperature increases with the decrease of heating period under constant pressure and increases with decreasing pressure for a constant heating time. A typical size of obtained monoclinic single crystal of cryolite is about \(2.0 \times 1.5 \times 0.8 \text{ mm}\).

Since the specific heat and the Raman spectrum for synthetic single crystals of cryolite are not available, the specific heat is measured by the differential scanning calorimeter and the Raman spectrum is taken by the Raman spectrometer. The obtained specific heat for the synthetic cryolite is expressed as a function of temperature:

\[ C_p = 183.9 + 141.9 \times 10^{-3}T. \]

The Raman spectra are assigned to the vibrational bands in the \(O_h\) point group of the isolated \(\text{AB}_6 (\text{AlF}_6^{2-})\) octahedron. By use of the assigned spectroscopic data and the Urey-Bradley force field, the force constants are calculated for the synthetic single crystal of cryolite. The force constants for the synthetic cryolite agree with those for the natural cryolite.

**Acknowledgments**

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**REFERENCES**


† Although the Raman band at \((10.25 \pm 0.15) \times 10^4 \text{ m}^{-1}\) might be interpreted as the combination, overtone or difference of the fundamentals, the assignment of this band is not possible at present. Further work is highly desirable.