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<td><strong>Author(s)</strong></td>
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Osaka University
Melting Points of Inorganic Fluorides†

Nobuya IWAMOTO*, Hideaki SUITO**, Shigeki HAMAMATSU*** and Ichiro SATOH****

Abstract
Measurements were made of the melting points of NaF, KF, MgF₂, and CaF₂ by means of thermal analysis. Puri-
fication of fluorides has been discussed.

1. Introduction
Recent technological advances, in both chemical and electrochemical processes involving fused salts at
high temperatures have resulted in an increased need for knowledge of the fundamental properties of the
melts. In the series of our investigation for the flux containing calcium fluoride by means of cryoscopic
studies, melting points of inorganic fluorides of high purity often varying significantly were measured with
high precision. These variations are caused by absorbed water due to an oxide formed on heating.

$$\text{MF}_2 + \text{H}_2\text{O} = \text{MO} + 2\text{HF}$$

Kojima et al. purified inorganic fluorides by passing anhydrous HF through the melts in order to
remove contaminating oxides. They found that melting points of fluorides purified were raised signifi-
cantly.

In the present work, commercial sodium fluoride and potassium fluoride of high purity were purified by
recrystallizing from slowly cooled melt (0.2–0.8 °C/min.) and selecting only clear crystal fragments
from the cooled ingot. It is possible by this method to remove impurities other than metal oxides caused
by absorbed water. With the purification of commercial calcium fluoride and magnesium fluoride, the
following two methods were chosen; firstly by heating to 500°C under a vacuum 10⁻³ torr over a period of 5
hrs and secondly by first treating NH₄FHF at 300°C and the heating to 800°C in graphite crucibles while
flushing with a dried argon stream.

2. Experimental
Materials: Commercial sodium fluoride (Wako Chem. A.R.) and potassium fluoride (Wako Chem.
A.R) were purified in graphite crucible which was heated before use in vacuo for approximately 8 hrs at
1400°C in a separate apparatus. After slow cooling (0.2–0.8°C/min.) in dry argon atmosphere, only clear
crystal fragments when cleaved to expose a fresh sur-
face were selected.

Commercial magnesium fluoride (Kanto Chem.
G. R.) and calcium fluoride (Kanto Chem. G.R.)
were purified in the following two methods; firstly by
heating to 500°C under a vacuum of 10⁻³ torr over a
period of 5 hrs and secondly by mixing NH₄FHF
thoroughly and heating to 300°C in graphite crucibles
and unreacted NH₄FHF and sorbed HF were driven
off by heating further at 800°C under continuous
argon flush until most of the excess NH₄FHF
vaporized.

Apparatus and Procedure: Melting points were
determined by the thermal arrests with the apparatus
described by Bell and Masson⁰ as shown in Fig. 1.
Melts were held in graphite crucible of dimention:
20 mm I. D. and 50 mm in depth with a re-entrant
well of dimensions 4 mm I. D. and 15 mm long,
which housed the junction of thermocouple.
Graphite crucibles were degassed at 1400°C in a sepa-
rate apparatus before used.
The Kanthal wire-wound alumina tube furnace
had a constant temperature hot zone (±0.5°C) of 6 cm
for the measurement of NaF and KF, and silicon
carbide (double spiral) resistance furnace had a con-
stant temperature hot zone (±0.5°C) of 4 cm for the
measurement of MgF₂ and CaF₂. The temperature
cycling of the furnace was limited to ±0.3°C by
means of Pt–13 % Rh thermocouple located close to
the winding and CHINO P. I. D. program controller.
Temperature were measured with a Pt–13 %Rh
thermocouple calibrated periodically against copper,
supplied by British Chemical Standards (m. p. 1083°C)
having the purity of 99.95 % . A charge of 10–13
grams of sample were placed in a graphite crucible
and argon was passed through at the rate of 100 cc/
min. after drying through phosphorous pentoxide.

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Seeds (100—50 mgs) were introduced by moving the soft iron slugs with a magnet as shown in Fig. 1. Rapid stirring technique has been used for the measurement of melting points of MgF₂ and CaF₂. The apparatus is shown in Fig. 2. Cooling curves were plotted manually every minute and the time between reading was one-half a minute whenever the charge was under going a phase change. Each measurement reported is the mean of at least 3 determinations at a suitable rate ranged from 0.2 to 0.8°C per minute in the liquid regions.

3. Results

Typical cooling curves obtained are shown in Fig. (a), (b), (c), and (d). When a pure component is cooled from the liquid state to its freezing point, latent heat is evolved at a constant temperature until solidification is complete; if the temperature of the specimen is read by potentiometer, it is observed to become constant for a definite time at the freezing point. However, because of supercooling with undesirable effect of lowering the temperature of the melt below the equilibrium temperature prior to the onset of solidification, equilibrium temperature is not able to obtain accurately in the case of sample with small heat of fusion. Supercooling depends upon the purity of the material, cooling rate and the nature of the system under investigation. It becomes less pronounced with the lower cooling rate. Although it was observed that the 'plateau' region in the temperature-time diagram increases with the lowering cooling rate, it is not still accurate to obtain the freezing point from the cooling curves as shown in Fig. 3 (b). It is therefore necessary to use techniques by stirring the melt, by bubbling inert gas through the melt or by seeding in which nucleation can be induced.

In the present investigation, seeding technique and rapid stirring technique have been used for measuring the freezing point with high precision. In seeding technique, seeds of weight 50—100 mgs were introduced at temperature of one degree centigrade lower temperature than that obtained without seeding in the cooling curve shown in Fig. 3 (b). (The same

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Melting Points of Inorganic Fluorides

![Graph showing cooling curves for pure NaF](image)

Fig. 3. Cooling curves for pure NaF.

a) 1.1 °C/min.  b) 0.29 °C/min.  c) 0.29 °C/min.  d) 0.29 °C/min.

Table 1. Melting points of inorganic fluorides.

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<td>NaF</td>
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An amount of seeds were introduced at higher temperature for comparison. After slight rise in temperature occurs as shown in Fig. 3 (c), a long, well-defined ‘plateau’ was obtained. Similarly, seeds were introduced at temperature of one degree centigrade higher temperature than that obtained in the cooling curves shown in Fig. 3 (b). After slight drop in temperature, a long, well-defined ‘plateau’ was obtained as shown in Fig. 3 (d). However, in the determination of melting points of MgF₂ and CaF₂, by this seeding technique, it was found difficult to obtain a long, well-defined ‘plateau’ as obtained in NaF and KF. Consequently melting points of MgF₂ and CaF₂ were determined by rapid stirring method. Melting points obtained were present in Table 1. The literature values in Table 1 are included to show the wide range of melting points in current use.

References