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Melting Points of Inorganic Fluorides†

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Abstract

Measurements were made of the melting points of NaF, KF, MgF_2 and CaF_2 by means of thermal analysis. Purification 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 proporties 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 varing significantly were measured with high precision. These variations are caused by absorbed water due to an oxide formed on heating.

$$MF_2 + H_2O = MO + 2HF$$

Kojima et al.[1] 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 significantly.

In the present work, commercial sodium fluodide and potasium 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^{-5} torr over a period of 5 hrs and secondly by first treating $NH_4F.HF$ 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 potasium 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 surface 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^{-5} torr over a period of 5 hrs and secondly by mixing $NH_4F.HF$ throughly and heating to 300°C in graphite crucibles and unreacted $NH_4F.HF$ and sorbed HF were driven off by heating further at 800 °C under continuous argon flush until most of the excess $NH_4F.HF$ vaporized.

Apparatus and Procedure: Melting points were determined by the thermal arrests with the apparatus described by Bell and Masson[2] as shown in **Fig. 1.** Melts were held in graphite crucible of dimentions of 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 separate 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 sprial) resistance furnace had a constant temperature hot zone (±0.5°C) of 4 cm for the measurement of MgF_2 and CaF_2. 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 grms. of sample were placed in a graphite crucible and argon was passed through at the rate of 100 cc/min. after drying through phosphorous pentaoxide.

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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 MgF_2 and CaF_2. 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 potentionmeter, it is observed to become constant for a difinite 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 ineart 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

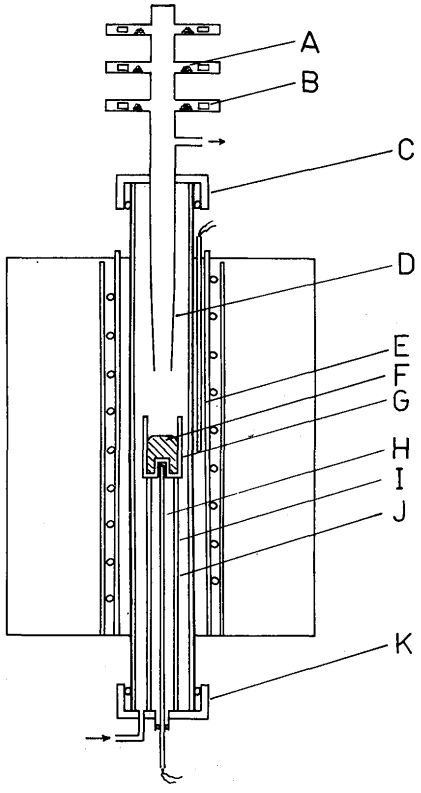

Fig. 1. Thermal analysis apparatus: A, seeds : B, iron slug. : C, water jacket. : D, quartz tubing. : E, T. C. tubing. : F, melt. : G, graphite crucible. : H, T. C tubing. : I, support tubing, : J, reaction tubing. : K, water jacket.

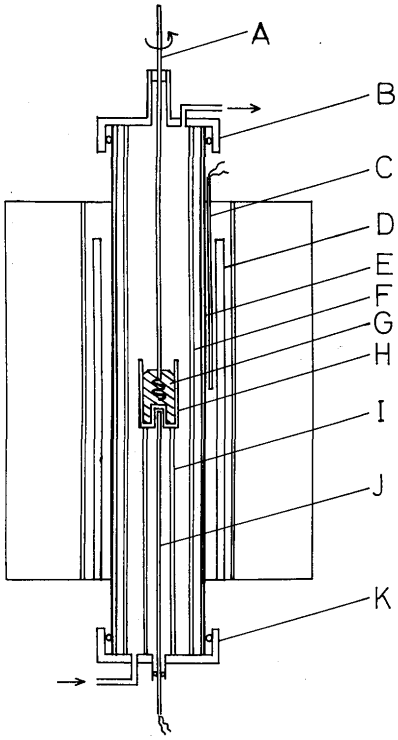

Fig. 2. Thermal analysis apparatus: A, graphite stirrer. : B, water jacket. : C, T. C. tubing. : D, SiC heating element. : E, reaction tubing. : F, reaction tubing. : G, melt. : H, graphite crucible. : I, support tubing. : J, T. C. tubing. : K, water jacket.

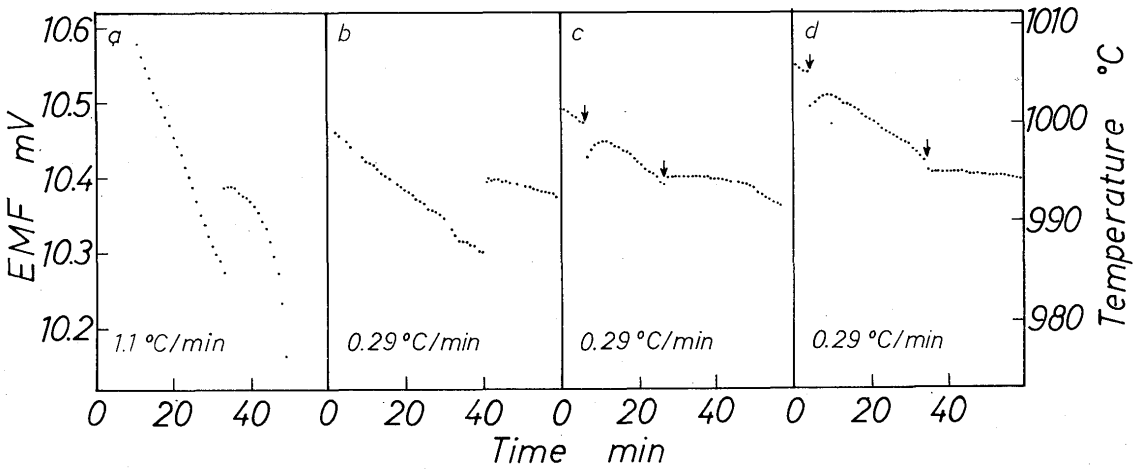

Fig. 3. Cooling curves for pure NaF.
a) 1.1 c/min. b) 0.29 c/min. c) 0.29 c/min. d) 0.29 c/min.

Table 1. Melting points of inorganic fluorides.

Temperature °C	Reference	
	NaF	
997	Landon and Ubbeloude	(3)
995	Eichelberger et al.	(4)
	Cantor	(5)
	Booth and Starrs	(6)
	Bredig et al.	(7)
	This Study (slow cooling)	
994	Porter and Brown	(8)
	Phillips et al.	(9)
	Brynestad et al.	(10)
	This Study (Wako)	
993	Kojima et al.	(11)
	MgF_2	
1263	Naylor	(15)
1261	Kojima et al.	(11)
1260	Tomlinson and Welch	(16)
	This Study	($NH_4F.HF$)
1258	This Study (10^{-5} torr and Kanto.)	
1255	Duncanson and Stevenson	(17)

Temperature °C	Reference	
	KF	
858	Porter and Brown	(8)
857	Kelley	(12)
	Westrum and Pitzer	(13)
856	Thoma	(14)
	This Study (slow cooling and Wako.)	
852	Kojima et al.	(11)
	CaF_2	
1423	Kojima et al.	(11)
1422	This Study	($NH_4F.HF$)
1421	This Study (10^{-5} torr and Kanto.)	
1420	Bååk and Ölander	(18)
	Gutt and Osborne	(19)
1419	Mukerji	(20)
1418	Naylor	(15)
1402	Porter and Brown	(8)

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. Similarlly, seeds were introduced at temperature of one degree centigrate 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 MgF_2 and CaF_2 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 MgF_2 and CaF_2 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.

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