STUDY ON PREPARATION OF BERYLLIUM FLUORIDE
-BY REACTION BETWEEN BEO AND NH_4F (OR NH_4HF_2)-

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I. Introduction

Recently some experimental data on the preparation of beryllium fluoride have been reported, of which wet process has been investigated frequently but dry process has never been done enough.

Beryllium fluoride is a very important material for production of metallic beryllium (a reactor material). And a high pure beryllium fluoride is required.

In this experiment the beryllium fluoride was produced by reaction between beryllium oxide and ammonium fluoride (or acidic ammonium fluoride), or dry process. The mechanism of the reaction, characteristic features of beryllium fluoride, and the behavior of impurities were investigated.

2. Experimental

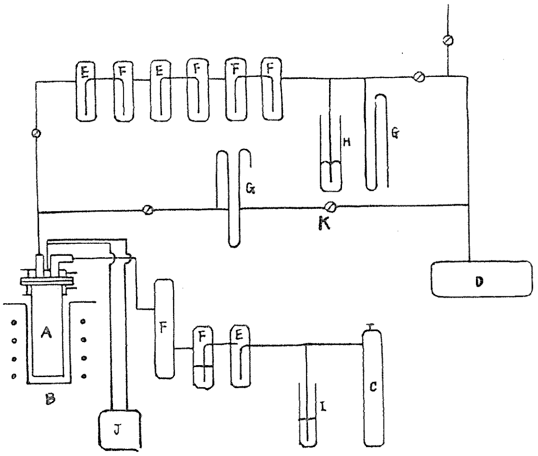
The reaction formulas between ammonium fluoride or a acidic ammonium fluoride and beryllium oxide etc. are as follows:

1. $BeO+2\,NH_4F \rightarrow BeF_2+2\,NH_3+H_2O$
2. $FeO+2\,NH_4F \rightarrow FeF_2+2\,NH_3+H_2O$
3. $1/3\,Fe_2O_3+2\,NH_4F \rightarrow 2/3\,FeF_3+2\,NH_3+H_2O$
4. $1/3\,Al_2O_3+2\,NH_4F \rightarrow 2/3\,Al_2F_3+2\,NH_3+H_2O$
5. $CaO+2\,NH_4F \rightarrow CaF_2+2\,NH_3+H_2O$
6. $MgO+2\,NH_4F \rightarrow MgF_2+2\,NH_3+H_2O$
7. $MnO+2\,NH_4F \rightarrow MnF_2+2\,NH_3+H_2O$
8. $PbO+2\,NH_4F \rightarrow PbF_2+2\,NH_3+H_2O$

1′. $BeO+NH_4HF_2 \rightarrow BeF_2+NH_2+H_2O$
2′. $FeO+NH_4HF_2 \rightarrow FeF_2+NH_3+H_2O$
3′. $1/3\,Fe_2O_3+NH_4HF_2 \rightarrow 2/3\,FeF_3+NH_3+H_2O$
4′. $1/3\,Al_2O_3+NH_4HF_2 \rightarrow 2/3\,AIF_3+NH_3+H_2O$
5′. $CaO+NH_4HF_2 \rightarrow CaF_2+NH_3+H_2O$
6′. $MgO+NH_4HF_2 \rightarrow MgF_2+NH_3+H_2O$
7′. $MnO+NH_4HF_2 \rightarrow MnF_2+NH_3+H_2O$
8′. $PbO+NH_4HF_2 \rightarrow PbF_2+NH_3+H_2O$

2.1. Experimental procedure

The experimrental apparatus is shown in Fig. 1, where A, E-F-C, E-F-D and K are a reaction retort, a cleaning system of argon gas, absorption and cleaning



A: Reaction retort
B: Electric furnace
C: Argon bomb
D: Vacuum pump
E, F: Absorption system
G: Pressure guage
H, I: Pressure controller
J: Pyrometer
K: Bypass tube

FIG. 1. Expermettal apparatus

system of produced matter and bypass tube. The experimental procedure was as follows: Charge the mixture of BeO and NH_4HF_2 into polyflon vessel and charge the vessel into the reaction retort. Pump the retort up to 10^{-3} mmHg and replace the space by argon gas. And let the first stage reaction occur at specified conditions, then let the second stage reaction (the thermal decomposition) occur at higher temperature under vacuum. After reaction, cool the retort to room temperature. And extract produced BeF_2 from the reaction product, filter and recrystallize BeF_2 in evaporating the solution extracted in polyflon beaker.

The experimental specified conditions were as follows.

a) Beryllium oxide used was 99% BeO with Fe, Al, Ca, Mg componsnts etc. NH_4F was extra chemical pure, and NH_4HF_2 was produced by distillation of the mixture of NH_4F+H_2O.
b) NH_4F or NH_4HF_2 to BeO were 1.5–3.5: 1 mol-ratio.
c) The reactions were: the first stage reaction 100°C and 1 2 hr, the second stage reaction (thermal decomposition) 250°C and 1–2 hr.

3. Experimental results

3.1. Yield percentage

Experimental results for production reaction were shown in Fig. 2–3. Fig. 2 shows the results of the reaction between BeO and NH_4F. The fact that the yield percentage in the case of using NH_4F with water was high, perhaps were due to NH_4F being activated as acidic ammonium fluoride partialy on account of water. Fig. 3 shows the results of the reaction between BeO and NH_4HF_2. The yield percentage of this experiment was almost about 100%.

3. 2. Behavior of imprities and X-ray diffraction test

Beryllium fluoride was extracted with water and after filtration recystalized by evaporation of the solution. In extraction with water and filtration, unsoluble imprities, Ca, Mg, were to be removed from BeF_2. And also SiF_4 was to be vaporized and removed in the second stage. The behavior of other impurities was

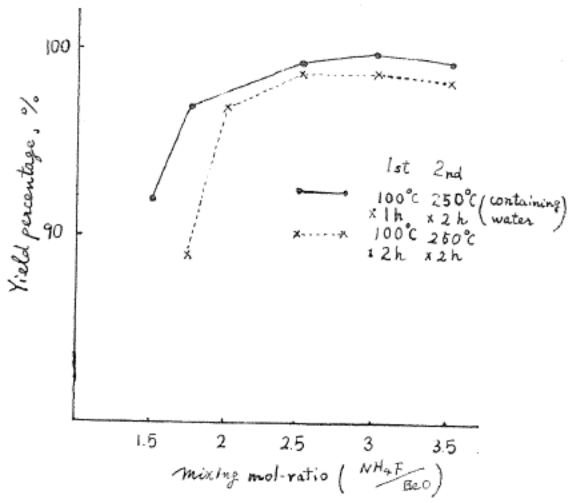


FIG. 2. The yield percentage in the case of NH_4F

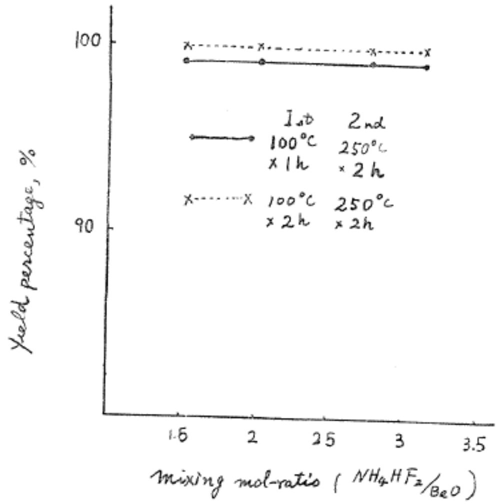


FIG. 3. The yield percentage in the case of NH_4HF_2

shown in Table 1. Iron content was lowered down to 1/8–1/10, and could be further decreased by controlling the pH of the solution. Lead content was all led into beryllium fluoride but removed by distillation purification of NH_4F or NH_4HF_2. Manganese content was lowered down to 1/3 (ac). Then Boron content that is no good for reactor material, and others were nigligihle trace values by spectrograph test.

In X-ray diffraction test, BeF_2 produced at 250°C (the second stage) and the mixing ratio 2 (NH_4HF_2 to BeO) was amorphous. In the case of mixing ratio 3, BeF_2 (produced at 250°C) was crystable and their peaks were the same as ASTM X-ray-card[3] of BeF_2 (Hexagonal) (as shown in Fig. 4). Further on heating the crystable sample at 300°C, under vacuum atmosphere, the peaks and background

TABLE 1. The behaviour of impurities

Sample	Impurity, ppm		
	Fe	Mn	Pb
BeO	870	600	0
NH_4F	40	0	1320
NH_4HF_2	645	0	0
BeF_2 (M)	170	250	1320*
BeF_2 (U)	85	125	1770*
BeF_2 (V)	110	200	1320*
BeF_2 (Y)	70	111	0**
Analytical method	Spectro-photometry	Spectro-photometry	Polarography

* Used NH_4F ** Used NH_4HF_2

Solubility of some fluorides to water[1]: CaF_2: 0.0016^{18}, 0.0017^{26}, NaF: 4.0^{15}, 4.3^{25},: MgF_2: 0.0087^{18}, AlF_3: 0.56^{25}, FeF_2: little PbF_2: 0.064^{20}, FeF_3: 0.091^{26}.

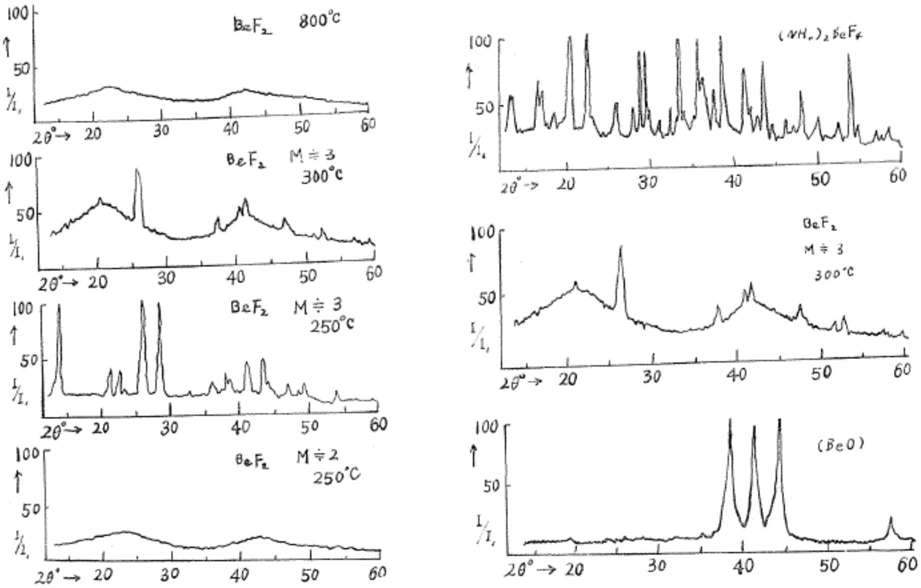


FIG. 4. X-ray Diffraction chart of some produced BeF_2, BeO, $(NH_4)_2BeF_4$

show semicrystable BeF_2. Then in heating it at 800°C the BeF_2 became also amorphous. And when there was a trace of NH_4F or $(NH_4)_2$ BeF_4 in BeF_2 produced BeF_2 showed the abnormal crystal lattice. Also the thermal analysis showed BeF_2 exactly, then we found that BeF_2 did not hydrate in water different from Meller's report.[2]

3.3. Chemical mechanism of the reaction

The production mechanism of beryllium fluoride is as follws: according to the results and the fact the BeF_2 produced in the excess of BeO to NH_4F_2 was produced through $(NH_4)_2\ BeF_4$ in the first stage;

1) Reaction between BeO and NH_4F;

$$\begin{array}{l} BeO+4\,NH_4F \rightarrow (NH_4)_2\ BeF_4+2\,NH_3+H_2O \\ (NH_4)_2+BeF_4 \rightarrow BeF_2+2\,NH_4F \\ \hline BeO+2\,NH_4F \rightarrow BeF_2+2\,NH_3+H_2O \end{array}$$

2) Reaction between BeO and NH_4F with water;

$$\begin{array}{l} 2\,NH_4F+H_2O\,(1) \rightarrow HN_4HF_2+NH_3+H_2O\ (g) \\ BeO+2\,NH_4HF_2 \rightarrow (NH_4)_2BeF_4+H_2O \\ (NH_4)_2BeF_4 \rightarrow BeF_2+2\,NH_4F_2 \\ \hline BeO+NH_4HF_2 \rightarrow BeF_2+NH_3+H_2O \end{array}$$

3) Reaction between BeO and NH_4HF_2;

$$\begin{array}{l} BeO+2\,NH_4HF_2 \rightarrow (NH_4)_2BeF_4+H_2O \\ (NH_4)_2BeF_4 \rightarrow BeF_2+2\,NH_4F_2 \\ 2\,NH_4F+H_2O \rightarrow NH_4HF_2+NH_3+H_2O \\ \hline BeO+NH_4HF_2 \rightarrow BeF_2+NH_3+H_2O \end{array}$$

4. Summary

1) BeF_2 was produced by the reaction between BeO and NH_4F or NH_4HF_2 at 100-250°C under specified conditions after extraction and refining with water, and recrystallized in polyflon vessel or beaker. And BeF_2 was improved by X-ray diffraction test and thermal analysis. The yield percentage in the case of using NH_4HF_2 was 99.99% and higher than in the case of NH_4F.

2) BeF_2 was extracted satisfactorily by water and not changed by water, ie, did not hydrate or not produced basic or oxyfluoride, and purified and recrystalized purely.

3) Chemical mechanism of the reaction between BeO and NH_4F or NH_4HF_2 was as follows: simply describing,

$$BeO+NH_4F\ (\text{or } NH_4HF_2) \xrightarrow[\text{(reaction)}]{100^\circ C} (NH_4)_2BeF_4 \xrightarrow[\text{(decomposition)}]{250^\circ C} BeF_2$$

Also the crystability of BeF_2 (produced) changed according to the reaction conditions and the impurities were pretty removed.

Aknowledgement

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Reference

1) Chemical Handbook (Maruzen) 1959.
2) T. W. Mellor: Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 11.

3) ASTM Card 10-88.
4) For Thermodynamic Calculation, Kubaschewski: Thermodynamic chemistry; White Burke: The Metal Beryllium; Quill: Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics.