

## Thermal decomposition of ammonium hexafluoroaluminate and preparation of aluminum fluoride

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**Abstract:** The thermal decomposition process of  $(\text{NH}_4)_3\text{AlF}_6$  was studied by DTA-TGA method and the related thermodynamic data were obtained. The results show that  $\text{AlF}_3$  is obtained after three-step decomposition reaction of  $(\text{NH}_4)_3\text{AlF}_6$ , and the solid products of the first two decomposition reactions are  $\text{NH}_4\text{AlF}_4$  and  $\text{AlF}_3(\text{NH}_4\text{F})_{0.69}$ , respectively. The three reactions occur at 194.9, 222.5 and 258.4 °C, respectively. Gibbs free energy changes of pertinent materials at the reaction temperatures were calculated. Enthalpy and entropy changes of the three reactions were analyzed by DSC method. Anhydrous aluminum fluoride was prepared. The XRD analysis and mass loss calculation show that  $\text{AlF}_3$  with high purity can be obtained by heating  $(\text{NH}_4)_3\text{AlF}_6$  at 400 °C for 3 h.

**Key words:** ammonium hexafluoroaluminate; thermal decomposition; aluminum fluoride; thermodynamic data

### 1 Introduction

Anhydrous aluminum fluoride is commonly used in the scientific experiments related to aluminum electrolyte. However, aluminum fluoride from most reagent companies contains crystal water because of its hydrometallurgical preparing process. Therefore, it is important to develop the process for preparing anhydrous aluminum fluoride in the laboratory.

If heating aluminum fluoride containing crystal water, alumina will be formed because of the hydrolysis reaction of aluminum fluoride. Sublimation process under vacuum is commonly used for preparing anhydrous aluminum fluoride [1–4]. But in this process, the experimental equipments are strictly required. TIE et al [5] have put forward a new process in which aluminum fluoride with crystal water is mixed with ammonium acid fluoride and the mixture is then heated. Hydrogen fluoride generated by the decomposition of ammonium acid fluoride will inhibit the hydrolysis of aluminum fluoride, so the purity of aluminum fluoride will increase. This process has also been used by other researchers [6–9]. SCHOLZ and KEMNITZ [10] have proposed a mechanochemical synthesis method to prepare aluminum fluoride with ammonium fluoride

used as fluorinating agent.

Anhydrous aluminum fluoride can be obtained by heating ammonium hexafluoroaluminate [11]. SHINN et al [12] have researched the thermal decomposition process of ammonium hexafluoroaluminate. According to their research results, ammonium hexafluoroaluminate decomposes by three steps.  $\gamma\text{-AlF}_3$  will be generated at 300 °C and then it will transform to  $\alpha\text{-AlF}_3$  at 720 °C. BECK et al [13] have studied the thermal decomposition process of ammonium hexafluoroallate and ammonium hexafluoroindate which has a similar crystal form to ammonium hexafluoroaluminate. The processes are proved to be carried out step by step, and the crystal transformation of the final fluoride product is also observed.

However, the researches mentioned above are focused on the crystal transformation of permanent materials, and the research on the thermal decomposition of ammonium hexafluoroaluminate is not systematic. Thermodynamic data of the decomposition and the preparation technology of anhydrous aluminum fluoride have not been involved.

In the present study, the thermal decomposition process of ammonium hexafluoroaluminate was analyzed in detail by comprehensive thermal analysis technique. The reaction equations were determined, and the pertinent

thermodynamic data were calculated. Subsequently, the process of preparing anhydrous aluminum fluoride in the laboratory was studied, and the reasonable preparing conditions were determined.

## 2 Experimental

The comprehensive thermal analysis experiments were carried out by a TA Instruments SDT 2960 thermal analysis instrument. The platinum crucible was used for holding samples.  $\alpha$ - $\text{Al}_2\text{O}_3$  after calcination was used as reference material. About 10 mg of the sample was used for each measurement. The experiments were carried out under argon shield and the flow rate was controlled to 20 mL/min.

In the study on preparation of anhydrous aluminum fluoride, ammonium hexafluoroaluminate was held in a graphite crucible which was placed in a resistance furnace, and the experiments were carried out under argon shield.

## 3 Results and discussion

### 3.1 DTA-TGA analysis on $(\text{NH}_4)_3\text{AlF}_6$

DTA-TGA experiments of  $(\text{NH}_4)_3\text{AlF}_6$  were carried out at four various heating rates of 1, 2, 5 and 10 °C/min, respectively. The scanned curves are shown in Fig. 1.

Each endothermic peak on the DTA curves in Fig. 1 corresponds to one step of decomposition reactions. There are three endothermic peaks on the DTA curves in Figs. 1(a), (b) and (c); but on the DTA curve in Fig. 1(d), only two endothermic peaks can be identified, which is attributed to that the heating rate is so high that the resolution of the curve is decreased. However, one can derive DTG curve from the TGA curve to improve the resolution. The turning points on the DTG curve are more easily to identify. DTG curve of  $(\text{NH}_4)_3\text{AlF}_6$  at heating rate of 10 °C/min is shown in Fig. 2. It is easy to identify that there are three obvious peaks on the DTG curve in Fig. 2, which correspond to the three steps of decomposition of  $(\text{NH}_4)_3\text{AlF}_6$ , respectively. Meanwhile, on all TGA curves in Fig. 1, there are four platforms, which also express the feature of three-step decomposition reactions.

The temperature corresponding to the extrapolated onset of peak on DTA or DTG curve is thought to be the starting temperature of the corresponding reaction. Therefore, the starting temperatures of the three-step decomposition reactions can be obtained by analyzing the DTA curves in Figs. 1(a)–(c) and DTG curve in Fig. 2.

The relationship curves between starting temperatures and heating rates are shown in Fig. 3. It can be seen in Fig. 3 that except for the second and third reactions corresponding to 5 °C/min of heating rate,

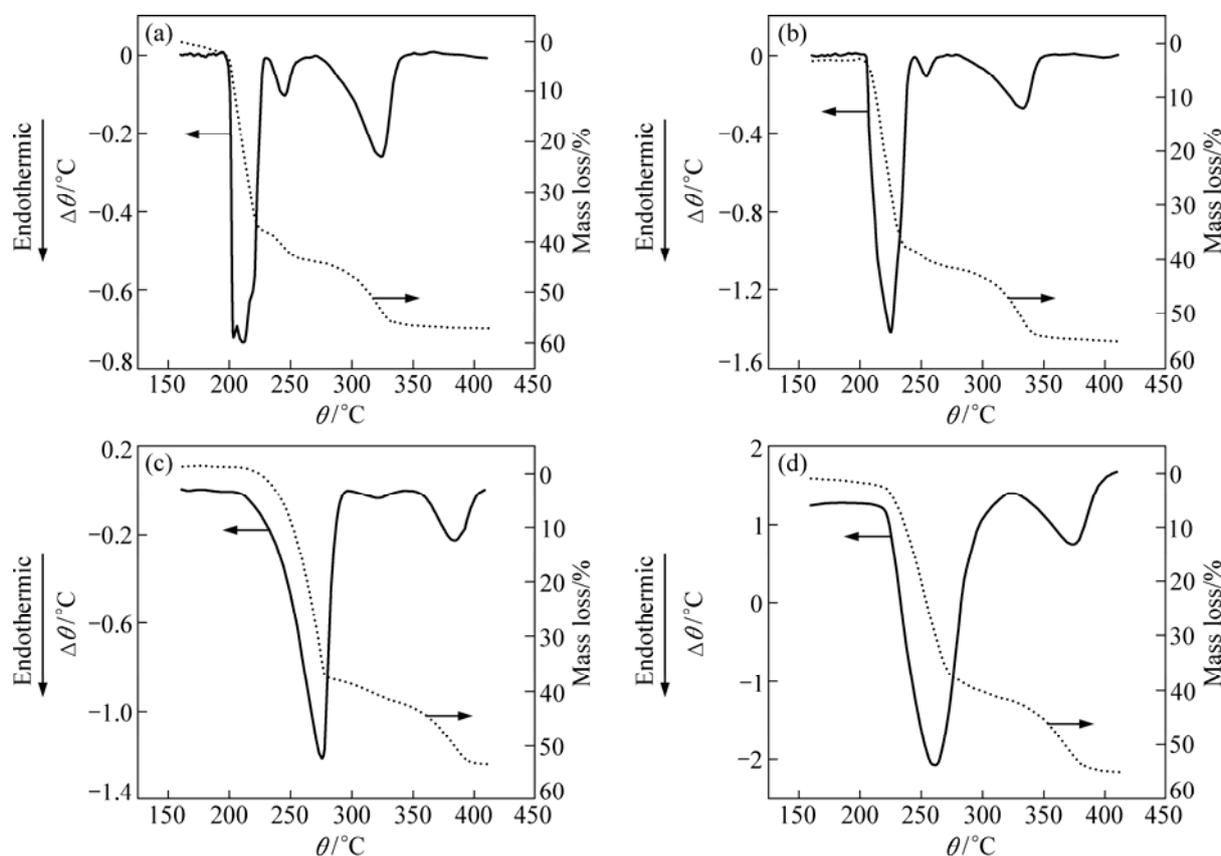


Fig. 1 DTA-TGA curves of  $(\text{NH}_4)_3\text{AlF}_6$  at different heating rates: (a) 1 °C/min; (b) 2 °C/min; (c) 5 °C/min; (d) 10 °C/min

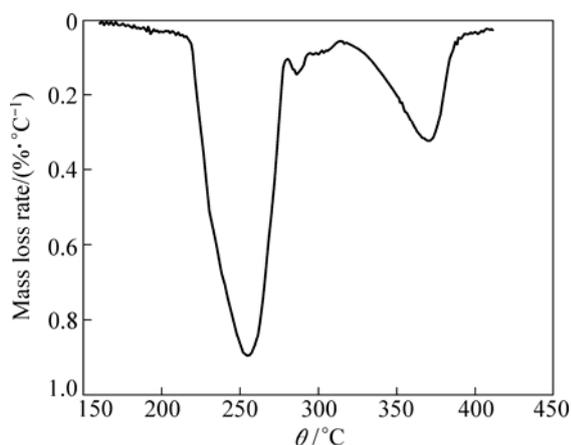


Fig. 2 DTG curve of  $(\text{NH}_4)_3\text{AlF}_6$  at heating rate of  $10\text{ }^\circ\text{C}/\text{min}$

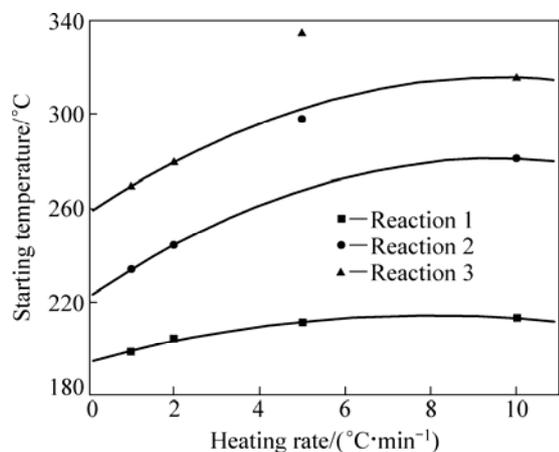


Fig. 3 Relationship between starting temperature and heating rate

there is a tendency that the starting temperature of the reaction is decreased with increasing the heating rate. For a lower heating rate, the heat transfer is more sufficient, so the whole system is closer to equilibrium. In contrary, for higher heating rate, the system is farther from equilibrium state, so the resolution of the instrument is decreased. The effect of heating rate on chemical reactions with mass change is more serious [14]. Therefore, it is thought that when the heating rate is equal to 0, the heat transfer is the most sufficient, and the whole system is the closest to heat equilibrium. Quadratic fit is made to the data points in Fig. 3 (the points corresponding to the second reaction and the third reaction for  $5\text{ }^\circ\text{C}/\text{min}$  of heating rate are not involved), as shown by the actual lines.

The extrapolated starting temperatures can be obtained by substituting the heating rate in the fitted equations with 0. The obtained starting temperature values are listed in Table 1.

$(\text{NH}_4)_3\text{AlF}_6$  will decompose during the heating process and  $\text{NH}_4\text{F}$  will be generated.  $\text{NH}_4\text{F}$  will further decompose to  $\text{HF}$  and  $\text{NH}_3$ . The other products of the

decomposition reactions of  $(\text{NH}_4)_3\text{AlF}_6$  will be the combination of  $\text{NH}_4\text{F}$  and  $\text{AlF}_3$  with different mole ratios or pure  $\text{AlF}_3$ . The three decomposition reaction equations can be obtained according to the mass loss of each reaction. It can be seen from the four TGA curves in Fig.1 that there is little effect of heating rate on mass loss. Therefore, in the present work, only the TGA curve of  $1\text{ }^\circ\text{C}/\text{min}$  is analyzed typically. The mass loss of each reaction is obtained from corresponding starting temperature of the next reaction. The temperature at which mass loss in the TGA curves does not change any more is used as that for the third reaction.

Table 1 Starting temperature and solid product of decomposition reactions of  $(\text{NH}_4)_3\text{AlF}_6$

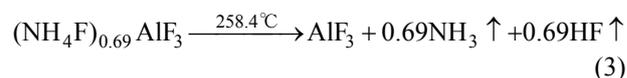
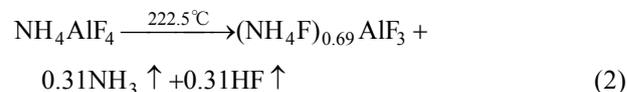
Reaction No.	Starting temperature/ $^\circ\text{C}$	Molecular formula of solid product
1	194.9	$(\text{NH}_4)_{0.97}\text{AlF}_{3.97}$
2	222.5	$(\text{NH}_4)_{0.69}\text{AlF}_{3.69}$
3	258.4	$\text{AlF}_3$

The amount of the mass loss equals that of  $\text{HF}$  and  $\text{NH}_3$ , which could be regarded as the amount of  $\text{NH}_4\text{F}$  according to stoichiometry. For 1 mol (195 g) of  $(\text{NH}_4)_3\text{AlF}_6$ , the mass of  $\text{NH}_4\text{F}$  can be obtained according to the mass loss of each decomposition, and then the amount of substance can be calculated. Based on the above results, the molecular formulas of the solid products of the three decomposition reactions can be obtained, which are also listed in Table 1.

In the solid product of the first decomposition reaction of  $(\text{NH}_4)_3\text{AlF}_6$ , the molar ratio between  $\text{NH}_4^+$  and  $\text{AlF}_4^-$  is 0.97. Considering the experimental error, the ratio is thought to be 1. Therefore, it is thought that the solid product of the first decomposition reaction is  $\text{NH}_4\text{AlF}_4$ .

The molecular formulas of the solid product of the second decomposition reaction is  $(\text{NH}_4)_{0.69}\text{AlF}_{3.69}$ . The molar ratio between  $\text{AlF}_3$  and  $\text{NH}_4\text{F}$  in the material is 1:0.69 according to stoichiometry. This material only exists at high temperature and its structure is very unstable [12].

Based on the above discussion, the three-step decomposition reaction equations are obtained as follows:



### 3.2 Gibbs free energy change of pertinent materials

It is thought that Eqs. (1)–(3) are at equilibrium state, that is, the Gibbs free energy change is 0.

Though there is no data on the Gibbs free energy changes of  $(\text{NH}_4)_3\text{AlF}_6$ ,  $(\text{NH}_4\text{F})_{0.69}\text{AlF}_3$  and  $\text{NH}_4\text{AlF}_4$  in the literatures, the Gibbs free energy change of the three materials at the reaction temperatures can be calculated based on Eqs. (1)–(3). The Gibbs free energy change of  $\text{AlF}_3$ ,  $\text{NH}_3$  and  $\text{HF}$  at the reaction temperatures can be obtained by using HSC Chemistry 5.1, as listed in Table 2. The calculated data of pertinent materials are also listed. During the calculation process, the Gibbs free energy changes of  $(\text{NH}_4\text{F})_{0.69}\text{AlF}_3$  at 258.4 °C and 222.5 °C are thought to be the same. Likewise, the Gibbs free energy changes of  $\text{NH}_4\text{AlF}_4$  at 222.5 °C and 194.9 °C are thought to be the same.

**Table 2** Gibbs free energy changes of pertinent materials in decomposition reactions of  $(\text{NH}_4)_3\text{AlF}_6$

Reaction No.	Material	$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$
	$\text{AlF}_3(\text{s})$	-1 551.881
Reaction 3 (258.4 °C)	$\text{NH}_3(\text{g})$	-151.223
	$\text{HF}(\text{g})$	-367.825
	$(\text{NH}_4\text{F})_{0.69}\text{AlF}_3(\text{s})$	-1 910.024
Reaction 2 (222.5 °C)	$\text{NH}_3(\text{g})$	-143.543
	$\text{HF}(\text{g})$	-361.017
	$(\text{NH}_4\text{F})_{0.69}\text{AlF}_3(\text{s})$	-1 910.024
Reaction 1 (194.9 °C)	$\text{NH}_4\text{AlF}_4(\text{s})$	-2 066.437
	$\text{NH}_4\text{AlF}_4(\text{s})$	-2 066.437
	$\text{NH}_3(\text{g})$	-137.713
	$\text{HF}(\text{g})$	-355.835
	$(\text{NH}_4)_3\text{AlF}_6(\text{s})$	-3 053.533

### 3.3 Enthalpy and entropy change of decomposition reactions of $(\text{NH}_4)_3\text{AlF}_6$

It is well known that the area of the peak enclosed by the DSC curve and the baseline is proportional to the enthalpy change as follows:

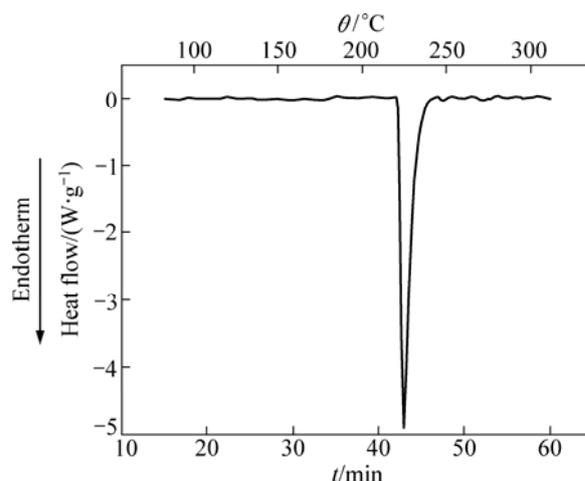
$$\Delta H = KA \quad (4)$$

where  $\Delta H$  is the enthalpy change in J/g;  $A$  is the area of the peak enclosed by the DSC curve and the baseline in J/g;  $K$  is the proportional constant, which needs to be calibrated by the reference material.

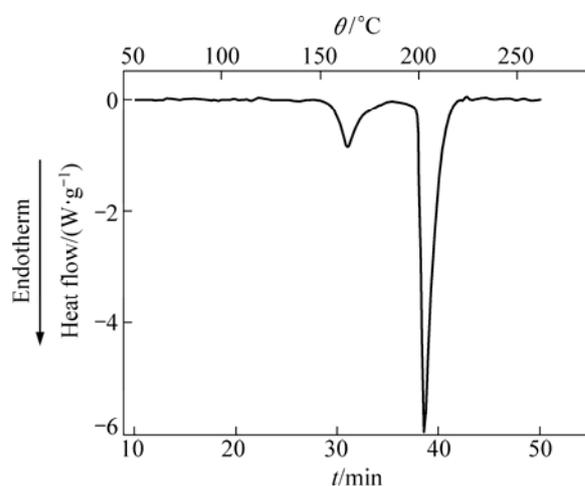
BREUER and EYSEL [14] have researched the checking standard materials for DSC experiments. In the present study, metallic Sn and  $\text{AgNO}_3$  are chosen to calibrate the value of  $K$ .

The heating rate of the DSC experiments was set to be 5 °C/min, the mass of both the two samples were as same as possible. The DSC curves of Sn and  $\text{AgNO}_3$  are shown in Figs. 4 and 5, respectively.

The endothermic peak on the DSC curve in Fig. 4 corresponds to the melting of Sn. On the DSC curve in



**Fig. 4** DSC curve of Sn at heating rate of 5 °C/min



**Fig. 5** DSC curve of  $\text{AgNO}_3$  at heating rate of 5 °C/min

Fig. 5, there are two endothermic peaks, and they correspond to the polymorphic transition and the melting of  $\text{AgNO}_3$ , respectively [15].

The calibration of  $K$  was carried out by the melting peaks of metallic Sn and  $\text{AgNO}_3$ . The values of  $K$  were calculated as 1.70 and 1.62, respectively. The difference between the two calculated values is small and the average value of 1.66 is used to calculate the enthalpy of decomposition reactions of  $(\text{NH}_4)_3\text{AlF}_6$ .

In the DSC measurement of  $(\text{NH}_4)_3\text{AlF}_6$ , the heating rate was also set as 5 °C/min and the mass used was as close to that of the former scanings as possible. The DSC curve of  $(\text{NH}_4)_3\text{AlF}_6$  is shown in Fig. 6.

By using Eq. (4), the enthalpy changes of the three decomposition reactions can be calculated and the results are listed in Table 3.

The relationships among entropy change, enthalpy change and Gibbs free energy change are described by

$$\Delta H = \Delta G + T\Delta S \quad (5)$$

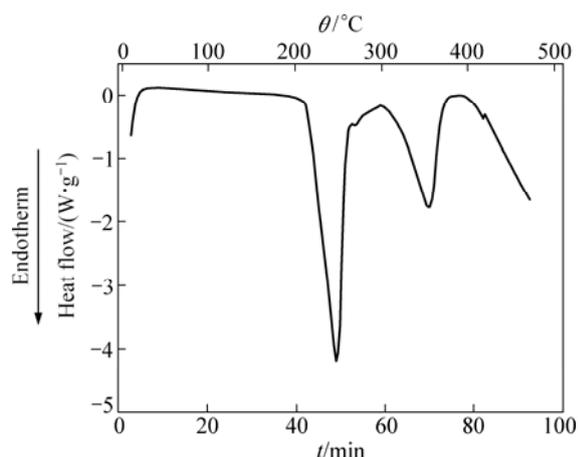


Fig. 6 DSC curve of  $(\text{NH}_4)_3\text{AlF}_6$  at heating rate of  $5^\circ\text{C}/\text{min}$

where  $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ , and  $T$  are the enthalpy change, Gibbs free energy change, entropy change, and temperature, and their units are  $\text{J}/\text{g}$ ,  $\text{J}/\text{g}$ ,  $\text{J}/(\text{g}\cdot^\circ\text{C})$ , and  $^\circ\text{C}$ , respectively.

Therefore, the entropy changes of the three decomposition reactions can be calculated and the results are also listed in Table 3.

Table 3 Enthalpy and entropy change of decomposition reactions of  $(\text{NH}_4)_3\text{AlF}_6$

Reaction No.	$\Delta H/(\text{J}\cdot\text{g}^{-1})$	$\Delta S/(\text{J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1})$
1	1734.9	3.72
2	6.1	0.01
3	1001.6	1.88

### 3.4 Preparation of anhydrous $\text{AlF}_3$ by heating $(\text{NH}_4)_3\text{AlF}_6$

According to the above thermal analysis of  $(\text{NH}_4)_3\text{AlF}_6$ , one will get anhydrous  $\text{AlF}_3$  if  $(\text{NH}_4)_3\text{AlF}_6$  is heated to a high enough temperature and held for a long enough time.

40 g of  $(\text{NH}_4)_3\text{AlF}_6$  was heated to  $400^\circ\text{C}$ , and then held for 3 h. The remained solid sample was 16.70 g, and the mass loss was calculated as 58.25%. Considering the error, it is thought that  $(\text{NH}_4)_3\text{AlF}_6$  is decomposed to  $\text{AlF}_3$  thoroughly.

The XRD pattern of the remaining sample is shown in Fig. 7. It indicates that the decomposition product is  $\text{AlF}_3$ . Therefore, it is thought that anhydrous  $\text{AlF}_3$  with high purity can be prepared by heating  $(\text{NH}_4)_3\text{AlF}_6$ .

## 4 Conclusions

1) During the heating process of  $(\text{NH}_4)_3\text{AlF}_6$ , three-step decomposition reactions occur as follows:

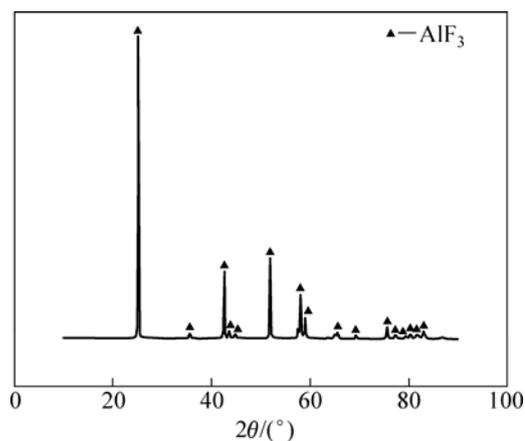
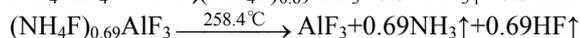
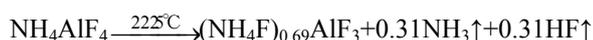


Fig. 7 XRD pattern of thermal deposition product of  $(\text{NH}_4)_3\text{AlF}_6$  at  $400^\circ\text{C}$

2) The Gibbs free energy changes of  $(\text{NH}_4)_3\text{AlF}_6$ ,  $\text{NH}_4\text{AlF}_4$ ,  $\text{AlF}_3(\text{NH}_4\text{F})_{0.69}$  at corresponding temperatures, and enthalpy and entropy changes of the three decomposition reactions are obtained.

3) High purity anhydrous  $\text{AlF}_3$  can be obtained by heating  $(\text{NH}_4)_3\text{AlF}_6$  to  $400^\circ\text{C}$  and maintaining for a long enough time.

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## 氟铝酸铵的热分解及氟化铝的制备

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**摘要:** 采用 DTA-TGA 法研究了  $(\text{NH}_4)_3\text{AlF}_6$  的热分解过程并获得了相关的热力学数据。结果表明,  $(\text{NH}_4)_3\text{AlF}_6$  经三步分解后, 固态产物为  $\text{AlF}_3$ , 前两步分解的固态产物分别为  $\text{NH}_4\text{AlF}_4$  和  $\text{AlF}_3(\text{NH}_4\text{F})_{0.69}$ , 三级反应的分解温度分别为 194.9, 222.5 和 258.4 °C; 计算了 3 个反应温度下相关物质的吉布斯自由能变化, 采用 DSC 法测量了 3 个反应的焓变和熵变。制备了无水氟化铝, XRD 分析和失重分析表明,  $(\text{NH}_4)_3\text{AlF}_6$  在 400 °C 下保温 3 h 可以得到高纯度的  $\text{AlF}_3$ 。

**关键词:** 氟铝酸铵; 热分解; 氟化铝; 热力学数据

(Edited by LI Xiang-qun)