The Mild Hydrothermal Synthesis of Complex Fluorides of $AZnF_3$ (A = Na , K)

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(Received June 16, 2000; CL-000596)

The complex fluorides of $AZnF_3$ (A = Na, K), which are isostructural with perovskite phases were obtained by the method of hydrothermal synthesis at 160–220 °C. Compared with traditional high-temperature solid-state method, the products were pure and contained lower amount of oxygen.

In recent years, there are many reports about the perovskite-type complex fluorides due to the interesting magnetic and optical properties. $KZnF_3$ is one of the important complex fluorides. In $KZnF_3$:Cr^{3+}, the output of laser has been achieved.[1] Several methods have been employed to synthesize $KZnF_3$, which required very rigorous equipment in the solid-state reaction at high temperature. Reports on the synthesis of $KZnF_3$ by high-temperature hydrothermal methods about 600 °C, 98MPa, have been acquired and are valuable,[2] but the reduced reactive temperature is desired. Hydrothermal synthesis under mild condition has been reported by Zhao et al.[3,4] With an aim towards a mild condition synthesis route to complex flourides, we studied the hydrothermal synthesis of $KZnF_3$ and $NaZnF_3$.

The starting materials for the synthesis of $AZnF_3$ were A_2CO_3 (A = Na, K) (A.R), ZnF_2 (A.R), HF (A.R), $(NH_4)HF_2$ (A.R) (all of reagent grade from Beijing Chemical Industries Co., Ltd., Beijing, China). Water was twice distilled. Under typical synthesis the mole ratios of the starting materials were 1.0 A_2CO_3: 1.0 ZnF_2: 1.0 $(NH_4)HF_2$. The typical synthesis procedure for crystalline $KZnF_3$ was as follows: 0.2073 g K_2CO_3, 0.1552 g ZnF_2 and 0.0856 g $(NH_4)HF_2$ were added to 8.0 mL water, the pH value of reaction mixture was about 7–8. Then, hydrofluoric acid was used to adjust the acidity of the mixture to the pH value about 3–4. The reaction mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 220 °C under autogenous pressure for 4 days; at the conclusion of the run, the autoclave was cooled in the air and decompressed. The contents were washed with deionized water and air-dried at room temperature.

All products were identified from X-ray powder diffraction on a Rigaku D/max-IIB diffractometer with a rotating target with Ni-filtered Cu Kα radiation at room temperature. The XRD data for index and cell-parameter calculations were collected by a scanning mode with a step of 0.02° and a scanning rate of 0.2° min^{-1} with silicon used as an internal standard. Observation of the crystallites by SEM was performed on a Hitachi X-650 scanning electron microscope. Thermogravimetric analysis was conducted using a TGS-2 thermogravimetric system.

The hydrothermal synthesis conditions were summarized in Table 1.

Table 1. Hydrothermal synthesis conditions for $KZnF_3$ and $NaZnF_3$

Starting materials		a : b		Reaction	Reaction	Phase in
a	b	mole rate	pH	Time /h	Temp./℃	product
K_2CO_3	ZnF_2	1 : 1	>7	96	220	No Product
K_2CO_3	ZnF_2	1 : 1	5-7	96	220	No Product
K_2CO_3	ZnF_2	1 : 1	3-4	96	220	$KZnF_3$
K_2CO_3	ZnF_2	1 : 1	3-4	72	220	$KZnF_3$
K_2CO_3	ZnF_2	1 : 1	3-4	120	160	$KZnF_3$
K_2CO_3	ZnF_2	1 : 1	3-4	96	120	No Product
K_2CO_3	ZnF_2	0.5:1	3-4	96	220	$KZnF_3$
K_2CO_3	ZnF_2	2 : 1	3-4	96	220	$KZnF_3$+KF
Na_2CO_3	ZnF	1 : 1	>7	96	220	No Product
Na_2CO_3	ZnF	1 : 1	2-3	96	220	$NaZnF_3$
Na_2CO_3	ZnF	2 : 1	2-3	96	220	$NaZnF_3$+NaF

The compositions of reactant and the pH value of the reaction system were found to be important to the formation, crystallization and purity of the products. The optimal ratio of the reactant was K : Zn = 2 : 1. The pH value of the reaction system, adjusted by hydrofluoric acid, was the key factor to the crystallization of the product. From the Table 1, we found that when the pH<7.0, the products formed gradually. However, when the pH value of the reaction system was more than 7.0, the degree of the crystallization was incomplete, and a mixture of $KZnF_3$ and ZnF_2 was produced. Therefore the optimal pH value of the reaction was about 3–4.

Crystallization time and temperature were the important factors for a successful synthesis, too. High temperature was a advantage factor to form the product. Although $KZnF_3$ could be crystallized at lower temperature, much reaction time was needed. High yield and pure product can be achieved when the reaction temperature is 220 °C and reaction time is about 4 days.

The optimal conditions of crystallization of $NaZnF_3$ were also studied. The best conditions of synthesizing $NaZnF_3$ were: Na^+:Zn^{2+} = 2:1, pH = 2–3, reaction temperature is 220 °C and reaction time is about 4 days.

The XRD pattern of products of the $KZnF_3$ and $NaZnF_3$ is shown in Figure 1.

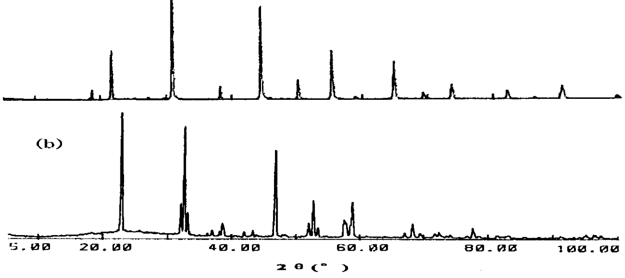
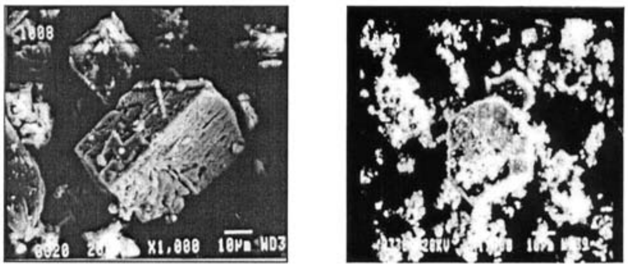


Figure 1. The XRD pattern of $KZnF_3$(a) and $NaZnF_3$(b).

From the Figure 1, we can find that the products which were obtained from hydrothermal crystallization were pure and no oxyfluoride peak, which usually occurs in solid-state reactions, is evident. The XRD patterns of $KZnF_3$ can be indexed in a cubic system, giving refined cell parameters a = 0.4058 nm. The value of the a is in satisfactory agreement with the value on the card of a = 0.4056 nm. While the XRD patterns of $NaZnF_3$ can be indexed in an orthorhombic system, giving a refined cell parameter a = 0.5570 nm, b = 0.7764 nm, c = 0.5402 nm, the value of the a is in satisfactory agreement with the value on the card of a = 0.5587 nm, b = 0.7775 nm, c = 0.5415 nm.



(a) (b)

Figure 2. The SEM photograph of $KZnF_3$(a) and $NaZnF_3$(b).

At room temperature, the morphology of the $KZnF_3$ and $NaZnF_3$ is observed from SEM. The photograph of the shape was shown in Figure 2. The shape of the crystal was cubic and the diameter of grain was about 50 µm, whereas the configuration of $NaZnF_3$ was octahedral and the diameter of the grain was about 40 µm.

The thermal stability of the product is studied by TG-DTA analyses in air. No phase transformation was observed up to 800 °C and no mass loss occurred for $AZnF_3$ between 50 °C to 650 °C, which indicates that the products are not hydrated and are stable in air.

Although inert gases were applied to protect products in solid-state synthesis, the content of oxygen was still very high. The oxygenous compounds may be formed in hydrothermal synthesis due to the similarity of the radius of F^- and OH^-. Therefore XPS was employed to discuss whether the product contains O^{2-} ion or OH^- and the results of the measurements were listed in Table 2. From Table 2, the values of F_{1s}, $Zn_{2p3/2}$ and Na_{1s} are calculated, compared the values of standard substance of ZnF_2, KF, NaF, typical bond of Zn–F, K–F, Na–F were confirmed to be formed while the bond of O–F, Zn–O, K–O, Na–O are not detected.

Table 2. The binding energy of XPS core level (eV) of $KZnF_3$ and $NaZnF_3$

Sample	$KZnF_3$	$NaZnF_3$	KF	NaF	ZnF_2
F_{1s}	685.10	685.40			
$Zn_{2p3/2}$	1022.70	1023.00			1022.80
$K_{2p3/2}$	293.20		293.10		
Na_{1s}		1072.40		1072.30	

In summary, the perovskite-type complex fluorides $KZnF_3$ and $NaZnF_3$ were synthesized by hydrothermal method under mild conditions. The pH value of the initial mixture, the molar ratio of the reactant, the reaction time and temperature dominate the crystallization of the product. Compared with traditional high-temperature solid-state method, the hydrothermal technique appears advantageous in terms of lower synthesis temperature, high purity and crystallinity with no evidence for insertion of oxygen.

This work was supported by the national key project of China for fundamental research.

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