Hydrothermal and Solvothermal Synthesis of the Complex Fluoride α′-$SrAlF_5$

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The complex fluoride α′-$SrAlF_5$ has been synthesized through hydrothermal and solvothermal methods under mild conditions. The effects of the molar ratio of starting materials, temperature, reaction time and solvents on the synthesis of α′-$SrAlF_5$ were discussed. The final products were characterized by XRD and SEM. The rod-like shape of α′-$SrAlF_5$ is shown in SEM images.

Keywords hydrothermal synthesis, solvothermal synthesis, complex fluoride, $SrAlF_5$

Introduction

Strontium aluminum pentafluoride-$SrAlF_5$ is a good host for the spectral research of doped rare earth ions due to its weak crystal field environment. For the first time, Hewes *et al.*[1] found the f→f line emission of the Eu^{2+} in $SrAlF_5$ matrix, and four nonequivalent sites for RE^{2+} in $SrAlF_5$ have also been reported.[2] The observation of the tunable-laser of Cr^{3+} from 852 to 947 nm in $SrAlF_5$ has attracted considerable attention[3] and the ferroelectric behavior[4] of $SrAlF_5$ has extended its applicable field. Two general methods, high-temperature solid state procedure and precipitation method, for synthesizing complex fluorides $SrAlF_5$ have been described.[5] The solid state method has the disadvantages of slow reaction rates and the high velocity of AlF_3 at temperatures approaching the melting points of the various compounds. On the other hand, a complicated set-up is required because of the corrosive nature of fluorides. The precipitation procedure need many trivial process, including the pH adjusting, heating, stirring and filtering, washing and drying. Mild hydrothermal and solvothermal synthesis, as a low energy-costing and less-pollution method, can enhance the reactivity of reactants in solution and can be used to prepare important crystalline solids, which are difficult to prepare or can not be prepared by solid state reactions. Such a reaction utilizes a solvent under pressure and at temperatures usually below its critical temperature under hydrothermal and solvothermal conditions. So far hydrothermal synthesis is successful for the preparation of important solids such as microporous crystals,[6] superionic conductors,[7] luminescent materials[8] *etc*. Li *et al.*[9] synthesized the semiconductor nanorod of CdE (E = S, Se, Te) by the solvothermal method. The new selenium-rich selenophosphate has also been reported in the same method as the above-mentioned. For complex fluorides, Zhao *et al.*[10] synthesized the complex fluorides by mild hydrothermal method, and showed the advantages of lower synthesis temperature, high-purity and crystallization with no evidence for insertion of oxygen. Recently Weil *et al.*[11] synthesized the (M, M′)AlF_5 (M, M′ = Ca, Sr, Ba) and refined their structures and obtained the monoclinic compound α′-$SrAlF_5$ and named the same compound synthesizing through high-temperature solid state way as β-$SrAlF_5$ with tetragonal type.

In this paper, the complex fluoride $SrAlF_5$ was synthesized through different solvents (including H_2O and organic solvents). The synthesis was studied from four aspects: the molar ratio of the starting materials, reaction time, reaction temperature and solvent. The final products were characterized by XRD and SEM.

Experimental

The preparation of $SrAlF_5$ was carried out in Teflon-lined stainless steel autoclave under autogenous pressure. The starting reactants were SrF_2 (A.R.), $AlF_3 \cdot 3.5H_2O$ (A.R.). The stoichiometric amounts of the reactant mixture were added into a Teflon-lined autoclave and filled with deionized water (hydrothermal) and ethanol, ethylene glycol, toluene, pyridine or tetrahydrofuran (solvothermal) above 85% whole capacity, respectively. Then the autoclave was sealed and kept at a certain temperature for several days. After the autoclave was cooled and depressurized naturally, the final powder products were washed with deionized water and dried in air ambient temperature.

The crystalline products were identified by X-ray

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diffraction on a Rigaku D/Max IIB using Cu $K\alpha_1$ (λ = 0.1541 nm) radiation with a step of 0.02° and a scanning rate of 0.2 (°)/min. Scanning electron micrographs (SEM) were performed on a Hitachi X-650B scanning electron microscope.

Results and discussion

Preparing condition

During the synthesis of $SrAlF_5$, the affecting factors such as the molar ratio of the starting materials, reaction temperature, reaction time and solvent were taken into consideration. The synthesis conditions for $SrAlF_5$ compounds by hydrothermal and solvothermal method are listed in Table 1 and Table 2.

For the hydrothermal synthesis, the mole ratio of the initial composition was found to be sensitive to the formation and purity of products. From Table 1, the slight excess of $AlF_3 \cdot 3.5H_2O$ has no obvious effect on the purity of products, but when the amount of SrF_2 was exceeded slightly, the impurity of SrF_2 phase occured, and the peak can be seen from XRD pattern, which may be resulted from the different solubility of $AlF_3 \cdot 3.5H_2O$ and SrF_2. The optimal ratio of SrF_2 and $AlF_3 \cdot 3.5H_2O$ is 1:1, which was used in the following investigation procedures.

Controlling the reaction time and starting materials ratio (1:1) stable, the effect of reaction temperature was investigated. All the results show that the lower the temperature, the longer the reaction time. When the temperature was below 200 ℃, the heterophase began to form and the complete heterophase at 160 ℃. Meanwhile we also found that, when the reaction temperature was lower than 200 ℃, the pure compounds of $SrAlF_5$ cannot be obtained even in a prolonged reaction time.

Keeping the temperature constant at 240 ℃, the hydrothermal treatment at different time (1 to 7 d) show no obvious effect on the crystallization. Fig. 1a is the XRD pattern of $SrAlF_5$ compounds synthesized at optimal conditions.

Table 1 Hydrothermal synthesis conditions for $SrAlF_5$

Starting materials a	Starting materials b	a:b (molar ratio)	pH	Reaction time (d)	Reaction temp. (℃)	Phases in product
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	1	240	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	3	240	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	5	240	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	7	240	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1.5	3	5	240	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1.5:1	3	5	240	$SrAlF_5 + SrF_2$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	5	200	$SrAlF_5$ + multiphase
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	9	200	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	5	160	multiphase

Table 2 Solvothermal synthesis conditions for $SrAlF_5$

Starting materials a	Starting materials b	a:b (molar ratio)	Reaction time (d)	Reaction temp. (℃)	Solvent	Phases in product
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	7	180	ethylene glycol	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	7	180	ethanol	SrF_2
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	7	180	pyridine	SrF_2
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	7	180	tetrahydrofuran	multiphase
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	7	180	toluene	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	1	180	ethylene glycol	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	3	180	ethylene glycol	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	5	180	ethylene glycol	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:2	5	180	ethylene glycol	$SrAlF_5$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:4	5	180	ethylene glycol	$SrAlF_5 + \beta\text{-}AlF_3$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:6	5	180	ethylene glycol	$SrAlF_5 + \beta\text{-}AlF_3$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1.5:1	5	180	ethylene glycol	$SrAlF_5 + SrF_2$
SrF_2	$AlF_3 \cdot 3.5H_2O$	2:1	5	180	ethylene glycol	$SrAlF_5 + SrF_2$
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	7	140	ethylene glycol	SrF_2
SrF_2	$AlF_3 \cdot 3.5H_2O$	1:1	9	140	ethylene glycol	$SrF_2 + SrAlF_5$

In the procedure of solvothermal synthesis, ethanol, ethylene glycol, toluene, pyridine and tetrahydrofuran were used as solvent respectively (Table 2). The results show that the pure products of $SrAlF_5$ can be synthesized using ethylene glycol or toluene as solvent at 180 ℃. There is no expected products when using the other three kind of solvents, only SrF_2 peak can be observed in XRD pattern, proving that there are no reaction happened in these solvents.

Changing the molar ratio of starting materials, the results show that the optimum value is 1∶1. When the molar ratio of $AlF_3 \cdot 3.5H_2O$ and SrF_2 was increased from 1 to 3, the peak of β-AlF_3 appeared in XRD pattern, if the molar ratio of SrF_2 and $AlF_3 \cdot 3.5H_2O$ was enhanced from 1 to 2, the peak of SrF_2 can be observed. In the following procedures, only ethylene glycol was used as solvent, and the molar ratio was kept at 1∶1.

Changing the reaction time (1—7 d), the pure products can be obtained routinely, and no obvious effect can be detected on the products, the experimental XRD pattern is in good agreement with the standard value.

When the reaction temperature was lowered to 140 ℃ with the reaction time of 7 d, only the SrF_2 peak can be seen from the XRD pattern. But if the reaction time was increased to 9 d, there were small amount of $SrAlF_5$ peak, showing that part of the reaction happened, in another word, with the lowering of the reaction temperature, the reaction was hard to carry on, and the longer reaction time was needed. Fig. 1b shows the XRD pattern of $SrAlF_5$ obtained from solvothermal procedure.

Comparing with the hydrothermal results, it can be seen that the pure phase of $SrAlF_5$ can be obtained under the lower reaction temperature when the organic solvents were used.

Characterization

Fig. 1 shows the powder XRD pattern of $SrAlF_5$ synthesized by hydrothermal (a) and solvothermal (b) method. The crystalline products show a good agreement with standard value (JCPDS No. 20-1193). According to literature,[2,11] the compound $SrAlF_5$ belongs to α′- and β-type synthesized through mild hydrothermal and high-temperature solid state method, respectively. So our samples should be the α′-$SrAlF_5$ with monoclinic crystal type.

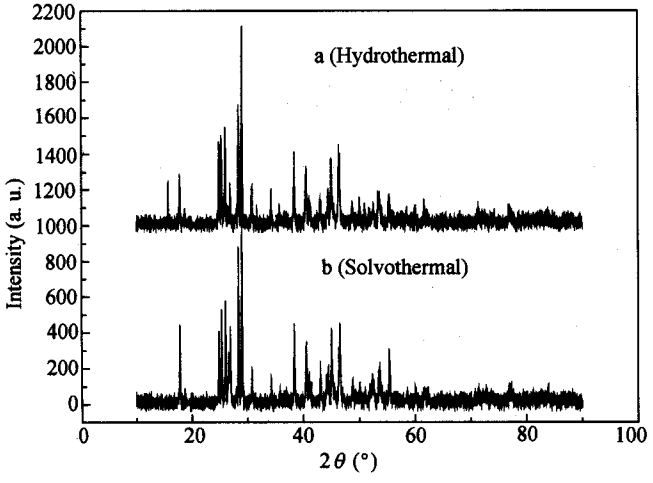

Fig. 1 XRD patterns of $SrAlF_5$.

The morphology of the samples synthesized from hydrothermal method was examined by SEM at room temperature, and the results are shown in Fig. 2. It could be seen that the crystals are homogeneous with rod-like shape, and at the end of the rod, the needle-like shape can be discerned. The average grain size of single-rod is *ca.* 6.8 μm. The SEM image of α′-$SrAlF_5$ synthesized from solvent procedure is given in Fig. 3. The rod-like shape can also be seen, but commonly they tend to aggregate together and to form larger rods, meaning that the crystals of α′-$SrAlF_5$ is easy to form an aggregated pattern or larger crystals in the existence of organic solvent. The average grain size of single-rod was *ca.* 13 μm, which is almost twice length of the product sizes synthesized from hydrothermal method. Compared with traditional high temperature solid-state methods, the hydrothermal and solvothermal synthesis method were used to synthesize complex fluoride appearing advantageous in terms of simple facility and operation, no corrosive nature, lower synthesis temperature, products single phase and well-crystallization.

Fig. 2 Representative SEM image of $SrAlF_5$ synthesized by hydrothermal method at 240 ℃ for 5 d.

Fig. 3 Representative SEM image of $SrAlF_5$ synthesized by solvothermal method.

Conclusion

In summary, the complex fluoride α'-$SrAlF_5$ was hydrothermally and solvothermally prepared under optimal conditions. Several factors, which may affect the formation and crystallization of α'-$SrAlF_5$ compounds, were investigated. The results show that the molar ratio of the starting reaction mixture and the reaction temperature are crucial in the hydrothermal synthesis. For the solvothermal procedure, besides the two factors above-mentioned, the type of solvent used is also an important affecting factor.

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