One-step synthesis of high-purity Li$_2$BeF$_4$ molten salt

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ABSTRACT

(NH$_4$)$_2$BeF$_4$ was synthesized and purified by recrystallization to remove sulfate ions before being used as the main raw material to prepare Li$_2$BeF$_4$ molten salt. (NH$_4$)$_2$BeF$_4$ was heated and melted with LiF at high temperature to produce Li$_2$BeF$_4$ molten salt without separate BeF$_2$ preparation by pyrolysis. The obtained salt has a melting point of 458–460 °C and an oxygen content below 500 ppm. The main impure metal ion and anion concentrations are less than 10 ppm and 80 ppm, respectively. This is a convenient, efficient and economical preparative method for high-purity Li$_2$BeF$_4$ molten salt.

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1. Introduction

Li$_2$BeF$_4$ (FLiBe) molten salt is applied mainly as a heat-transfer medium in nuclear reactors, solar thermal power generation and high-energy batteries. Because of its excellent physical and chemical properties, especially its low absorption and activation neutron characteristics, it is known as "the neutron-transparent fluoride" and is the first choice as molten salt and primary coolant in nuclear reactors [1,2]. FLiBe molten salt of high purity is required in nuclear reactors, because its physical and chemical properties, such as melting point, viscosity, radiation stability and fuel salt dissolution ability, depend largely on FLiBe molten salt purity. For example, oxygen in molten salt usually reacts slowly with nuclear fuel to form a paste or results in UO$_2$ and ThO$_2$ deposition in the reactor. This decreases nuclear fuel solubility, and results in local loop overheating and other serious consequences. In addition, there is a limited number of elements with high neutron absorption cross-section and strong corrosive oxygen ions in FLiBe molten salt [3,4].

High purity BeF$_2$ is one of the main raw materials used to prepare FLiBe molten salt. However, it is unavoidable that the prepared BeF$_2$ contains sulfate ions, because sulfuric acid leaching of beryllium is an indispensable process during the production of BeF$_2$. Sulfate ions are corrosive and the main carriers of oxygen in molten salt, and need to be removed in FLiBe molten salt

preparation. Most methods developed and tested at Oak Ridge National Laboratory for the removal of sulfate ions and oxide impurities from fluoride salts are based on high-temperature treatment with H$_2$ and HF gas mixtures [5–8]. However, this requires considerable expenditure on special equipment, monitoring systems and personnel safety since HF is extremely corrosive, H$_2$ is flammable and explosive, and the reaction time is more than 70 h. For the preparation of small batches of salts, this process is not justified economically. Therefore, a new preparation method is essential to obtain high-quality FLiBe molten salt under mild, laboratory conditions.

We used a "source control" strategy to remove sulfate ions in (NH$_4$)$_2$BeF$_4$, which is the precursor of BeF$_2$, by repeated recrystallization. (NH$_4$)$_2$BeF$_4$ and LiF were heated and melted in a molar ratio of 33.3:66.7. High-purity FLiBe molten salt was synthesized at high temperature by a one-step method. This method eliminates the need for a separate process to prepare BeF$_2$ and for a long time to treat molten salt with H$_2$–HF. During (NH$_4$)$_2$BeF$_4$ decomposition, HF is generated and is used to reduce the oxygen content in the FLiBe molten salt. This method has many advantages, such as mild reaction conditions, simple operation, low equipment requirements, good economy and low risk (Scheme 1).

2. Results and discussion

2.1. Recrystallization of (NH$_4$)$_2$BeF$_4$

In crystal form, (NH$_4$)$_2$BeF$_4$ exists as a three-dimensional network composed of tetrahedral BeF$_4^{2-}$ linked to one another,

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$$(NH_4)_2BeF_4 + LiF \xrightarrow[- NH_3, - HF]{Neat, \triangle} Li_2BeF_4$$
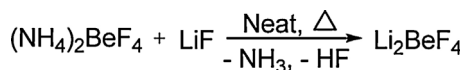
Scheme 1. One-step Li_2BeF_4 synthesis.

and the electric charge, shape and crystal size of the BeF_4^{2-} are very similar to SO_4^{2-} [9]. This suggests that BeF_4^{2-} and SO_4^{2-} possess crystallographic isomorphic properties and cause crystal mixture precipitation of BeF_4^{2-} and SO_4^{2-} during recrystallization. Recrystallization conditions need to be optimized to obtain high crystallinity and high purity $(NH_4)_2BeF_4$.

$(NH_4)_2BeF_4$ is soluble in water, and insoluble in solvents such as ethanol, methanol, acetone and ethyl acetate. We added 17% ($v_{solvents}$:v_{water} = 1:5) non-aqueous solvents into water to form mixed solvents, and $(NH_4)_2BeF_4$ recrystallization was carried out in these mixed solvents. To study the impact of non-aqueous solvents on $(NH_4)_2BeF_4$ yield and SO_4^{2-} removal efficiency, 75 °C was chosen as the initial crystallization temperature, the cooling rate was set to 4 °C h^{-1} and the final temperature was 5 °C, with the results shown in Table 1. All experiments were repeated three times, and the results of SO_4^{2-} content are presented as mean ± standard deviation (SD). When these nonelectrolytes are added to the salt-water system, the water molecules prefer to be surrounded by nonelectrolyte molecules rather than electrolyte ions, which leads to a decrease in proportion of "free water". The links between salt and water molecules therefore weaken, salts are transported far from the water molecules and gather together, and this results in over-saturation and precipitation [10,11]. If we consider the yield of $(NH_4)_2BeF_4$ and the removal efficiency of SO_4^{2-}, an ethanol–water mixed solvent was chosen as the recrystallization mixed solvent. Compared with a single water solvent, the $(NH_4)_2BeF_4$ solubility is lower in the ethanol–water mixed solvent, and this type of solvent can yield stable $(NH_4)_2BeF_4$ crystal shapes.

During recrystallization, the cooling rate of saturated solution was found to be crucial to the product crystal size and purity. Different cooling rates were tested to study their influence on impurity removal efficiency. Determination the content of sulfate
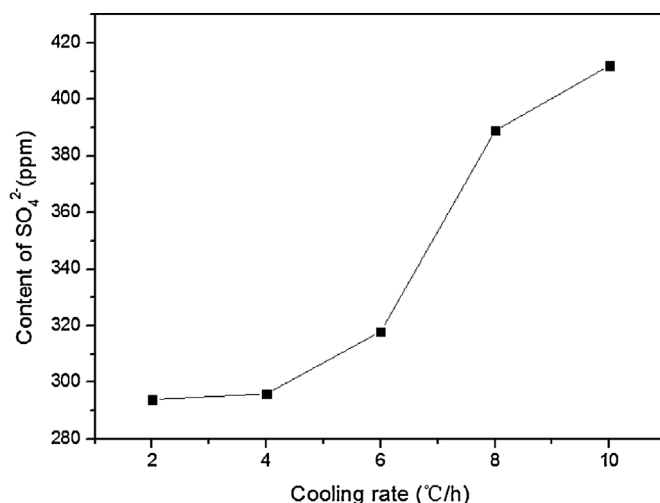

Fig. 1. The cooling rate dependence of the content of SO_4^{2-} in $(NH_4)_2BeF_4$ after recrystallization using ethanol–water mixed solvent. Determination the content of sulfate ion in $(NH_4)_2BeF_4$ by ion chromatography.

ion in $(NH_4)_2BeF_4$ by ion chromatography (IC). It can be seen from Fig. 1 that the SO_4^{2-} content in prepared $(NH_4)_2BeF_4$ decreases significantly with decrease in cooling rate. The $(NH_4)_2BeF_4$ crystal size increases and becomes more regular at a slow cooling rate (Fig. 2). The crystals prepared at lower cooling rate (<4 °C h^{-1}) were rod-like and columnar with low impurity content. If the cooling rate is too rapid (>8 °C h^{-1}), many small crystals that contain large amounts of impurities form. The crystals are small acicular particles. Because the rate of cooling is rapid, solution suddenly enters the unstable region, and causes explosive nucleation. As a result, impurities (such as SO_4^{2-}) are trapped in the crystals.

Based on these factors, $(NH_4)_2BeF_4$ recrystallization was carried out in a 5:1 water:ethanol solution at an initial recrystallization temperature of 75 °C, a terminal temperature of 5 °C and a cooling rate of 4 °C h^{-1}. The product was purified by two recrystallizations under the same conditions. The final S and SO_4^{2-} contents were 17 ppm and 58 ppm, respectively. The content of other impurities was less than 50 ppm (Table 2). The X-ray diffraction (XRD) pattern of $(NH_4)_2BeF_4$ is shown in Fig. 3 and can be indexed in the orthorhombic crystal system. Values for $(NH_4)_2BeF_4$ are similar to those of the corresponding $(NH_4)_2BeF_4$ [JCPDS Card 01-084-0142, a_0 = 7.65, b_0 = 5.93, c_0 = 10.46]. Using high-purity $(NH_4)_2BeF_4$ as raw material, a single crystal of $(NH_4)_2BeF_4$ was grown from aqueous solution by slow evaporation at room temperature [12,13]. The crystal data and number of reflections are summarized in Table 3. The powder XRD patterns and crystal data show that no detectable impurities were present in the samples, which indicates that the products were single phase.
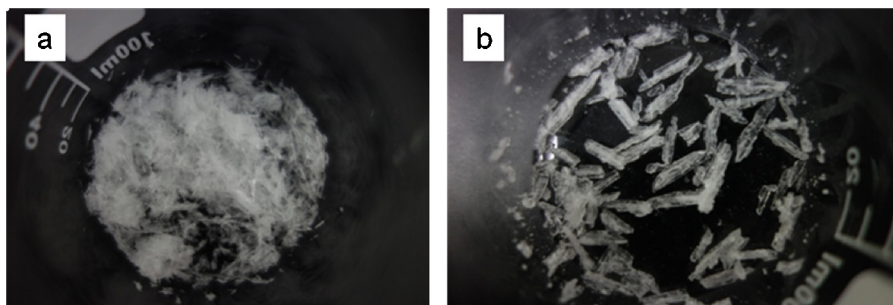
Table 1
Purification results of $(NH_4)_2BeF_4$ by the recrystallization method with different solvents. The results of SO_4^{2-} content are presented as mean ± standard deviation (SD).

	Content of SO_4^{2-} (SD) (ppm)	Solubility (g)	Yield (%)
Raw material	1279	–	–
Water	408 (3)	47.12	35
Ethanol–water mixed solvent	318 (2)	45.52	38
Methanol–water mixed solvent	334 (3)	40.51	43
Acetone–water mixed solvent	385 (5)	51.88	43
Ethyl acetate–water mixed solvent	383 (1)	45.07	28

Fig. 2. The appearance of $(NH_4)_2BeF_4$ after recrystallization using ethanol–water mixed solvent with different cooling rate (cooling rate >8 °C h^{-1} (a) and <4 °C h^{-1} (b)).