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Synthesis of LaF_3 superfine powder by microwave heating method①

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Abstract: LaF_3 superfine powder was synthesized from $La(CH_3COO)_3$ and NH_4F by microwave heating method, using ethanol or pure water as dispersants respectively. The results of XRD and SEM indicate that the superfine powder has high purity, regular particle shape and narrow distribution of granularity. The granularity of the best sample is in the range of 100－200 nm. The influence of different dispersants on the crystal degree and microstructure was discussed. After the superfine powder was formed into a slice at pressure of 25－60 MPa, its electrochemical impedance spectroscopy was tested by electrochemical impedance spectroscopy(EIS) measurement. The result shows that the grain refining of LaF_3 powder increases its ionic conductivity. Compared with traditional preparation methods of LaF_3 powder, the advantages of microwave heating method were summarized.

Key words: LaF_3; superfine powder; microwave; electrochemical impedance spectroscopy; ionic conductivity
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1 INTRODUCTION

LaF_3 is one of the most important solid electrolytes with high ionic conductivity. LaF_3 superfine powder is widely used to make F_2, CO, O_2, SO_2, CO_2 gas sensors and La sensor in order to test the different gases concentration and the activity of La in the melt respectively[1, 2]. LaF_3 superfine powder is also used as the additive in the lubricants so as to increase the anti-wear properties at extreme pressure and lubricating ability[3]. The anti-wear properties of some alloys can be reinforced with LaF_3 superfine powder as the additive. Furthermore, LaF_3 superfine powder is one of the vital materials for laser crystal[4, 5].

However, the preparation of LaF_3 superfine powder is not easy because of its typical ionic bond. Generally, LaF_3 powder is prepared by adding lanthanum oxide or lanthanum carbonate powder into hydrofluoric acid at room temperature. Also, LaF_3 powder is prepared by heating lanthanum oxide and ammonium bifluoride powder. In this experiment LaF_3 superfine powder was synthesized from $La(CH_3COO)_3$ and NH_4F by microwave heating method, using ethanol or pure water as dispersants.

2 EXPERIMENTAL

$La(CH_3COO)_3$ powder and NH_4F powder were equally mixed with mole ratio of 1∶3, using ethanol or pure water as dispersants respectively, and the mixture was ground in the ball miller for 6－12 h. The two samples were heated in microwave furnace with 200 W power respectively. The course of reaction was obtained by weighing the samples every 2 min during the reaction. X-ray diffraction(XRD) experiments were performed using D/max-rA X-ray diffractometer(30 kV, 10 mA) with Cu (λ= 1.54 Å) irradiation at a scanning rate of 0.02(°)/s in the 2θ range of 20°－70°. The microstructure of the different superfine powders was observed using JSM-5800 scanning electron microscope. The influence of different dispersants on the grain size and microstructure was discussed.

The superfine powder prepared using ethanol as dispersant was formed into a slice at a pressure of 25－60 MPa. Aluminum foils used to be electrode lines were washed with ethanol and hydrochloric acid. At 19.7 ℃, the electrochemical impedance spectroscopy of the slice was tested by PARM378 electrochemical impedance spectroscopy (EIS) measurements of EG&G Co. Ltd., USA. According to the electrochemical impedance spectroscopy simulated by Z-view software, the slice impedance was calculated.

3 RESULTS AND DISCUSSION

3.1 Reaction process

LaF_3 superfine powder was synthesized from $La(CH_3COO)_3$ and NH_4F by microwave heating method. The reaction is

$$La(CH_3COO)_3 + 3NH_4F = LaF_3 + 3NH_3\uparrow +$$

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$3CH_3COOH \uparrow$ (1)

By weighing the sample every 2 min during reactions, it was found that when pure water was used as dispersant, most of the reaction happened in the initial 12 min. If heating time last, the quality of the sample kept invariable. When ethanol was used as dispersants, most of the reaction happened in the initial 8 min. If heating time last, the quantity of the sample kept invariable. Therefore, the heating time of the samples corresponding to ethanol and pure water as dispersants was set 15 min and 10 min respectively.

The reaction time with ethanol as dispersant is shorter than that with pure water. According to the microwave heating theory[6], the speed of warm-up temperature for the sample is

$$\frac{\Delta T}{t} = \frac{\sigma E^2}{\rho c_p} \quad (2)$$

where σ is the thermal conductivity, ρ is density, c_p is the molar heat capacity at constant pressure and E is the electric field intensity. If E keeps invariable, since

$$\sigma_{ethanol} > \sigma_{water},\ \rho_{ethanol} < \rho_{water},\ c_{p,\ ethanol} < c_{p,\ water}$$ [7]

So

$$\frac{\sigma_{ethanol} E^2}{\rho_{ethanol} c_{p,\ ethanol}} > \frac{\rho_{water} E^2}{\rho_{water} c_{p,\ water}}$$

Then

$$\frac{\Delta T}{t_{ethanol}} > \frac{\Delta T}{t_{water}}$$

Therefore, the heating speed with ethanol as dispersant is faster than that with pure water as dispersant.

3.2 X-ray diffraction analysis

The XRD patterns of synthesized superfine powder using ethanol and pure water as dispersants are shown in Fig. 1. It can be seen from Fig. 1 that:

1) These two kinds of synthesized superfine powders were proved to be LaF_3. Dispersants have a strong impact on the acuity of diffraction peaks. The diffraction peaks of the sample using pure water as dispersant are very wide. The reason may be that the crystal LaF_3 superfine powder grows faultily or that some amorphous material comes into being. Contrarily, the diffraction peaks of the sample with ethanol as dispersant are very sharp. It indicates that ethanol can improve the growth of the crystal LaF_3 superfine powder.

2) In general, it is easy for LaF_3 to be hydrolyzed into LaOF in moist atmosphere. But, no diffraction peaks of LaOF can be seen in Fig. 1(a). The reason is that the $La^{3+} - H_2O$ bond is weakened by microwave, which makes $La(H_2O)_9^{3+}$ dehydrate more easily. So the naked La^{3+} can combine with F^- directly[6].

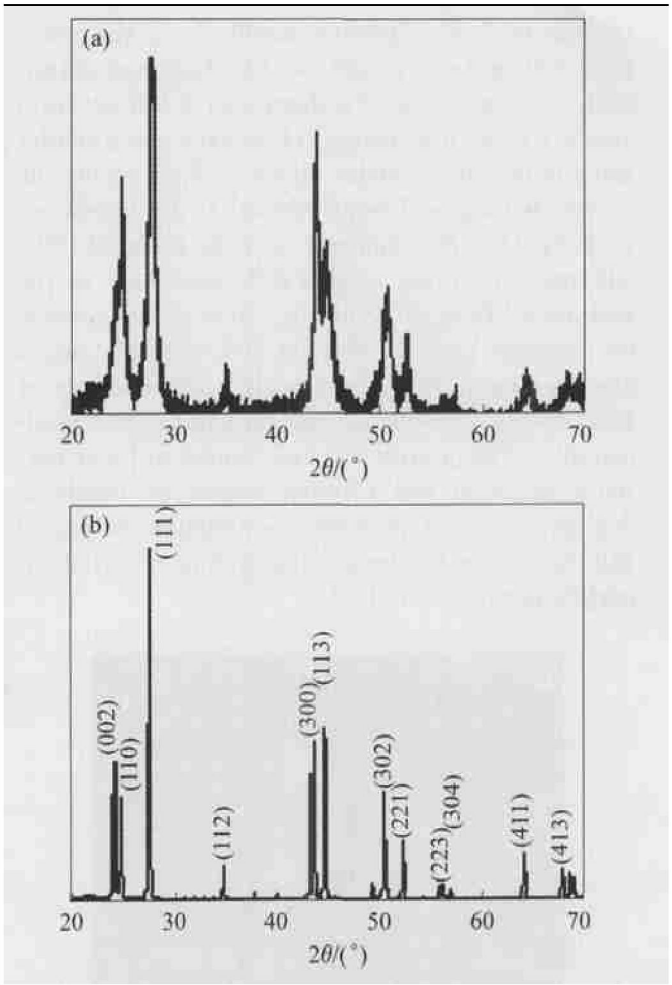

Fig. 1 XRD patterns of LaF_3 superfine powders
(a) —With pure water as dispersant;
(b) —With ethanol as dispersant

3) LaF_3 belongs to hexahedral crystal system. The lattice constants can be calculated by the formula of hexahedral crystal gap and Brug equation[8]:

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4(H^2 + K^2 + HK)}{3a^2} + \frac{L^2}{c^2}\right] \quad (3)$$

where λ is the wavelength; θ is the diffraction angle; H, K and L are crystal indexes. According to the two peaks of (300) and (302) in XRD pattern shown in Fig. 1, the lattice parameters are obtained as shown in Table 1.

Table 1 Lattice parameters of synthesized samples and standard LaF_3

Lattice constant	By Fig. 1(a)	By Fig. 1(b)	Standard LaF_3
a/ Å	0.717 6	0.719 5	0.718 6
c/ Å	0.726 8	0.735 4	0.735 2

3.3 Microstructure analysis

Figs. 2(a) and (b) show the SEM images of synthesized LaF_3 superfine powders using pure water or ethanol as dispersant respectively. It is indicated that when pure water is used as dispersant, the size of

LaF_3 superfine powder is in the range from 100 nm to 1 μm and the distribution of granularity is asymmetric. Furthermore, a few aci form crystals come into being. However, the granular distribution and powder shape of LaF_3 superfine powder synthesized using ethanol as dispersant are very regular. The diameter is in the range of 100 – 200 nm. The cause of this difference may be the hydroxy of H_2O molecules has more higher reactivity than the hydroxy of C_2H_5OH molecule and is attracted by cations more easily. The hydroxy of H_2O molecules will become directional and readjustable. The interior H_2O molecules will lose partial translation and rotation degree of freedom. Another cause is that the combination of partial H_2O molecules accelerates the agglomeration of superfine powder particles[6].

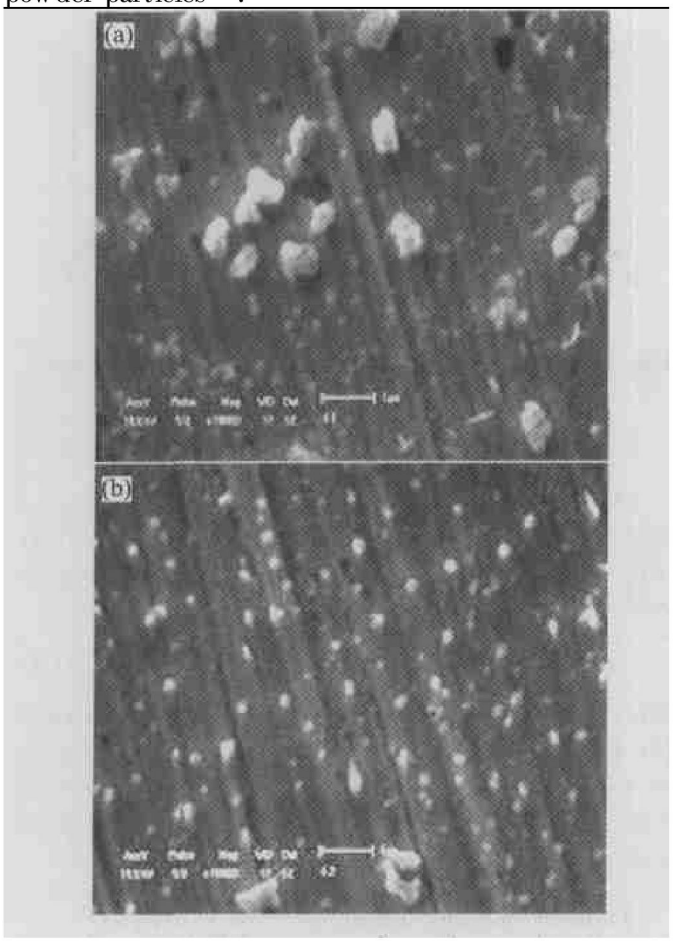

Fig. 2 SEM images of synthesized LaF_3 superfine powder
(a) —With pure water as dispersant;
(b) —With ethanol as dispersant

3.4 Electrochemical impedance spectroscopy

The superfine powder prepared using ethanol as dispersant was formed into a slice at a pressure of 25 – 60 MPa. The slice EIS spectrum (at 19.7 ℃) is shown in Fig. 3. According to the approximate semicircle figure of EIS, an equivalent circuit is designed as shown in Fig. 4. In this equivalent circuit, R_s presents the crystal grain resistance, which is the left

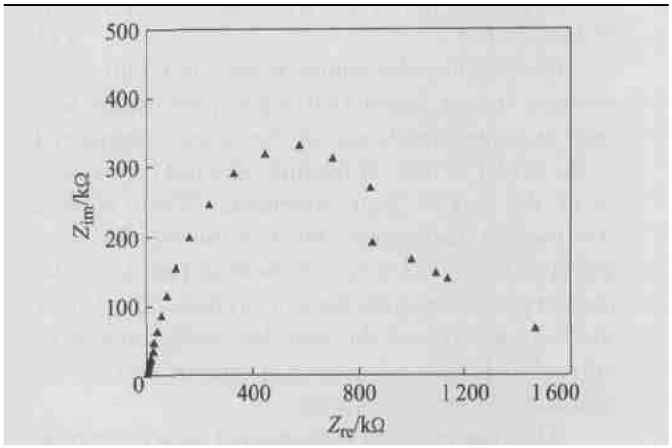

Fig. 3 EIS spectrum of slice

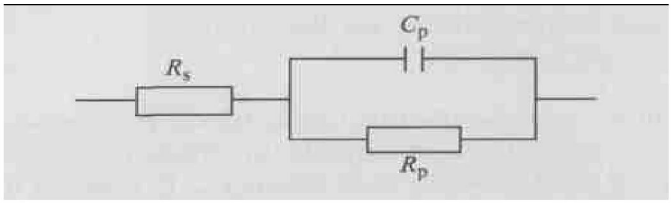

Fig. 4 Equivalent circuit of slice

crossover point of the approximate semicircle and X axes, R_s is small enough to be neglected; R_p and C_p present the grain boundary resistance and capacitance respectively. The value of $R_s + R_p$ equals the right intersection of the approximate semicircle and X axes. The electrode process is actually controlled by electric charge transfer in the electrodes and electrolyte interfaces[9-11]. According to Z-view software, the calculation of the slice impedance is $R = R_p \approx 1.42 \times 10^6$ Ω (at 19.7 ℃). The ionic conductivity corresponding to the slice of LaF_3 is calculated by the formula as

$$\sigma = \frac{l}{RS} \tag{4}$$

where σ is the ionic conductivity, R is the impedance, l is the thickness and S is area.

When $l = 1.4 \times 10^{-1}$ cm, $S = 28 \times 10^{-2}$ cm^2, the calculated result is $\sigma = 3.52 \times 10^{-7}$ S/cm. The ionic conductivity of LaF_3 single crystal is about 10^{-7} S/cm[12]. It is proved that the grain refining of LaF_3 improves its ionic conductivity. The reason may be that every superfine powder particle has the ideal single crystal properties[13]. Once so many small single crystals are formed into a slice, the electrochemical properties of every particle and the whole slice change unexpectedly. As to how to explain its mechanism more profoundly, more research should be done in future.

3.5 Comparison of microwave heating method with traditional preparation methods

The traditional preparation methods of LaF_3

powder are listed as below:

$$La_2O_3 + 6HF = 2LaF_3 + 3H_2O \quad (5)$$

$$La_2(CO_3)_3 + 6HF = 2LaF_3 + 3CO_2 + 3H_2O \quad (6)$$

$$La_2O_3 + 6NH_4HF_2 = 2LaF_3 + 6NH_3 + 3H_2O + 6HF \quad (7)$$

In reactions (5) and (6), HF is reactant. The SEM image of LaF_3 powder prepared by reaction (5) is shown in Fig. 5. As seen from Fig. 5, LaF_3 powder is all strip particles, whose average granularity is 5 - 10 μm.

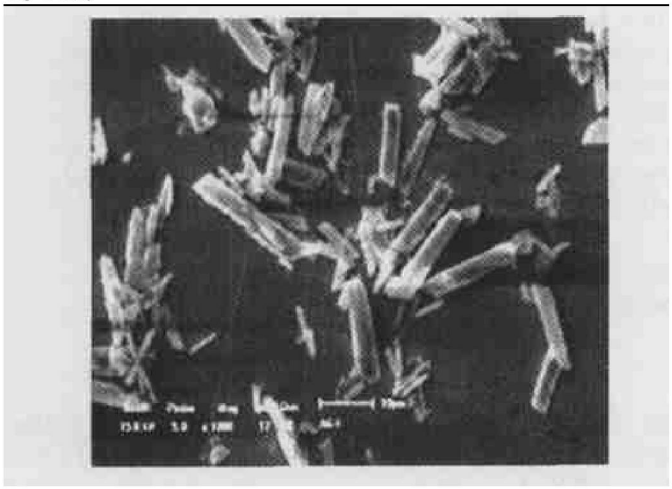

Fig. 5 SEM image of LaF_3 powder prepared by reaction (5)

In reaction (7), there is poisonous HF giving off. This reaction should be heated in alloy tube and kept at 300 ℃ for 12 h. When the reaction is over, superfluous NH_4HF_2 and vapor should be expelled. In a word, these traditional reactions are all related to poisonous HF and pollute environment. Compared to these traditional preparation methods of LaF_3 powder, the microwave heating method has a lot of advantages such as short reaction time, low energy consumption; high purity and small, well-distributed granularity of resultant.

4 CONCLUSIONS

1) LaF_3 superfine powder was synthesized from $La(CH_3COO)_3$ and NH_4F by microwave heating method, using ethanol or pure water as dispersant respectively.

2) The results of XRD and SEM indicate that LaF_3 superfine powder has high purity, regular particle shape and narrow distribution of granularity. Ethanol as dispersant has a great impact on LaF_3 grain size and microstructure.

3) LaF_3 superfine powder was formed into a slice. Its electrochemical impedance spectroscopy was tested by EIS measurements(at 19.7 ℃). The ionic conductivity of LaF_3 was calculated. The result shows that the grain refining of LaF_3 powder increases its ionic conductivity.

4) Compared with the traditional preparation methods of LaF_3 powder, microwave heating method has a lot of advantages such as short reaction time, low energy consumption, high purity and small, well-distributed granularity of resultant.

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