ISSN : 0974 - 7486 Volume 7 Issue 6

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(6), 2011 [387-390]

Synthesis of LaF_3 superfine powder by microwave heating method

S.G.Gaurkhede[*1], M.M.Khandpekar[2], S.P.Pati[3]

[1]Department of Physics, Bhavans College of ASC, Andheri (W) Mumbai-58 (INDIA)

[2]Material Research Lab, Department of Physics, Birla College, Kalyan – 421304 (INDIA)

[3]Department of Physics, Sambalpur University, Jyoti Vihar, Burla-768019, Orissa (INDIA)

Received: 19th April, 2011 ; Accepted: 19th May, 2011

ABSTRACT

LaF_3 superfine powder was synthesized from $LaCl_3.7H_2O$ and NH_4F by microwave method, using methanol or de-ionized water as dispersants respectively. The results of XRD, TEM, 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 10-20nm. Compared with traditional preparation methods of LaF_3 powder, the advantages of microwave heating method was summarized. The powder belong to hexagonal symmetry with a =7.182 A.U, and c = 7.254 A.U. Rapid synthesis with near uniform diameter of lanthanide based nano crystals has been achieved.

KEYWORDS

$LaF_{3;}$
Superfine powder;
Microwave;
Granularity.

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 addictive in the lubricants to increase the antiwear properties at extreme pressure and lubricating ability[3]. The antiwear properties of some alloys can be reinforced with LaF_3 superfine powder as addictive. 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. In addition, LaF_3 is prepared by heating lanthanum oxide and ammonium bifluoride powder. In this experiment LaF_3 superfine powder was synthesized from $LaCl_3.7H_2O$ and NH_4F by microwave heating method, using methanol or de-ionezed water as dispersants.

EXPERIMENTAL

The received chemicals were used without further purification. The synthesis of LaF_3 nanocrystalline was carried out in domestic microwave, which was operated at 100% power of 800W and a frequency of 2.45 GHz. In a typical procedure for the preparation of LaF_3 powder 0.072 g of NH_4F 0.192 mol was dissolved in 10 ml of de-ionized water. Another solution was prepared by mixing 7 ml of 0.064 mol $LaCl_3.7H_2O$, and swiftly injected into the NH_4F solution through 10 ml

Full Paper

syringe. White precipitate appeared instantly. The mixture was put in a 100 ml round beaker and placed in microwave. The synthetic reaction was carried out at 800 W for 1 hr with on-off mode having a time interval of 30 sec. Initial milkfish white indicating formation of LaF_3. The white precipitate then segregated to the bottom. The separated product was then washed several times with water and absolute alcohol and dried at room temperature.

The X-ray crystallographic pattern was obtained by PANALYTICAL XPERT PROMPD diffractometer model using Cu Kα =1.54 Å with scanning rate of 2° per min from 0° to 80°. The morphology and particle size analysis of the sample prepared were done by using transmission electron microscope (Philips, CM 200, operating voltage:20-200kv, resolution: 2.4A°). The morphology and elemental composition of materials was examined by HR-SEM WITH EDAX–WDS analysis with Quanta FEG 200 with Pt coating.

RESULTS AND DISCUSSION

Reaction process

LaF_3 superfine powder was synthesized from $LaCl_3$.7H2O and NH_4F by microwave heating method. The reaction is Proportion of La^{3+} ions can be related by the chemical reaction equation below.

$$X LaCl_3.7H_2O + 3NH_4F \rightarrow La_xF_3 + 3NH_4Cl + 7H_2O$$

Here, x represents the molar percentage of La^{3+} ions, where X=0.064 mol and 0.192 mol of NH_4F. Solutions containing Molar Proportions [X (1): NH_4F (3)]

The reaction time with methanol as dispersant is shorter than that with de-ionized water. According to the microwave, heating theory[6]. The Speed of warm up temperature for the sample is $\frac{\Delta T}{t} = \frac{\sigma E^2}{\rho C_p}$ where σ is the thermal conductivity, ρ is the density, C_p is the molar heat capacity at constant pressure, and E is the electric field intensity. If E is keeps invariable, since

$$\frac{\sigma_{methanol} \rangle \sigma_{de-water} \quad \rho_{methanol} \langle \rho_{de-water}}{C_{p\ methanol} \langle C_{p\ de-water}} \quad [7]$$

$$\text{so} \quad \frac{\sigma_{methanol} E^2}{\rho_{methanol} C_{p\,methanol}} \rangle \frac{\sigma_{de-water} E^2}{\rho_{de-water} C_{p\ de-water}}$$

Then $\frac{\Delta T}{t_{methanol}} \rangle \frac{\Delta T}{t_{de-water}}$

Therefore, the heating speed with methanol as dispersant is faster that de-water as dispersant.

X-ray diffraction analysis

The XRD patterns of the synthesized superfine powders using methanol and de-ionized water as dispersants are shown from the Figure 1(a) and (b) that:

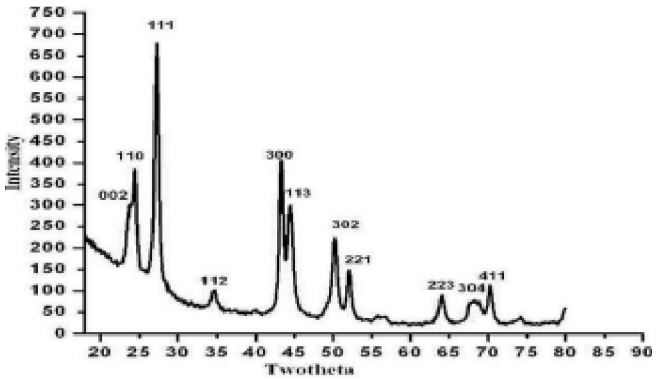

Figure 1(a) : XRD Pattern of LaF_3 de-waters.

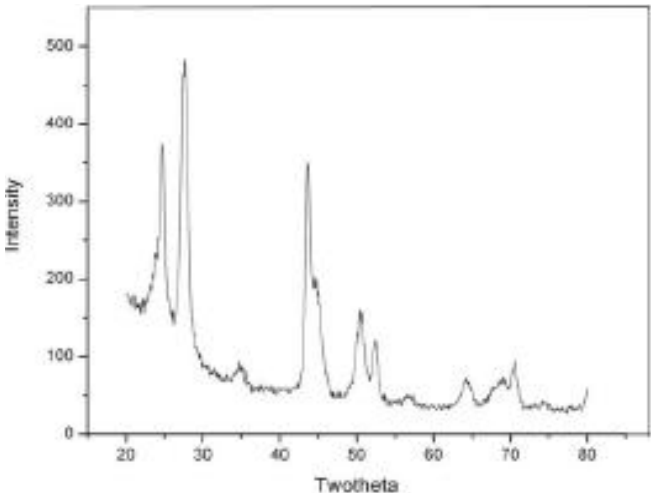

Figure 1(b) : XRD Pattern of LaF_3 methanol.

These two kinds of synthesized superfine powders were proved to be LaF_3. Dispersants have strong impact on the acuity of diffraction peaks. The diffraction peaks of sample using pure water as dispersant are very wide. The reason may be that the crystal LaF_3 superfine powders grow 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.

In general, it is easy for LaF_3 to be hydrolyzed into

LaOF in moist atmosphere. However, no diffraction peaks of LaOF can be seen. The reason is that the La^{3+}- H_2O bond is weakened by microwave, which makes $La(H_2O)_9^{3+}$ dehydrate more easily. Therefore, the naked La^{3+} can combine with F directly[6].

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

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

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 Figure 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 Figure 1(a)	By Figure 1(b)	Standard LaF_3
a/A^0	7.182	7.195	7.186
c/A^0	7.254	7.34 2	7.352

Microstructure analysis

Figures 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 1μm 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

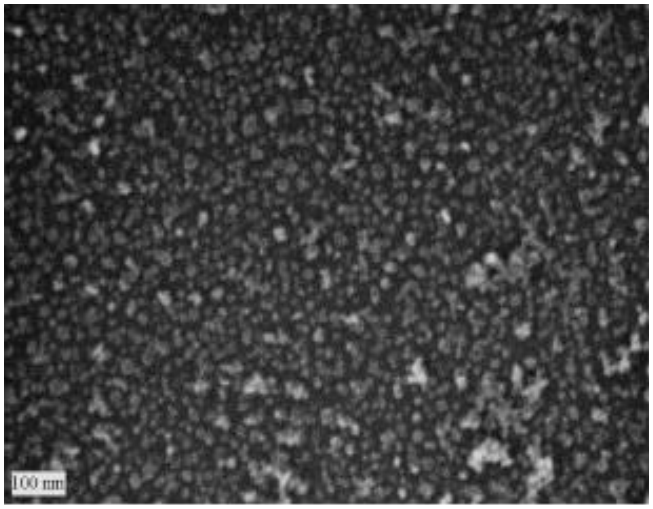

Figure 2(a) : SEM image of LaF_3 de-waters.

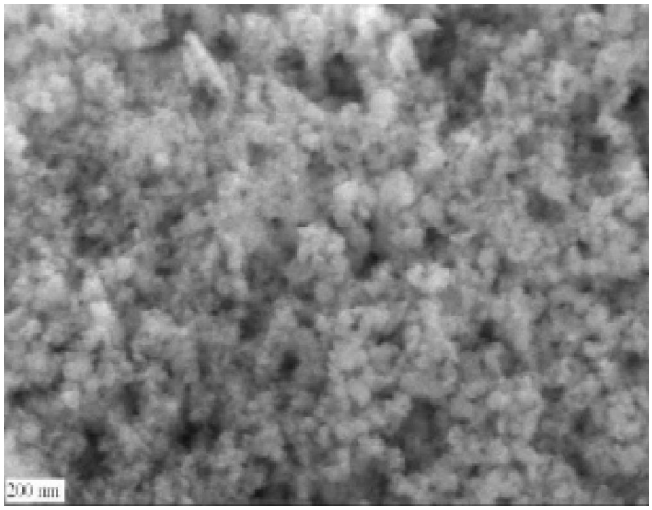

Figure 2(b) : SEM image of LaF_3 methanol.

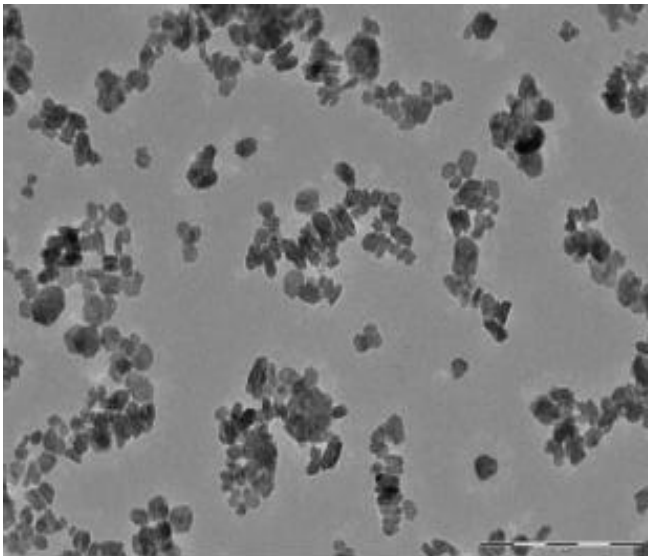

Figure 3(a) : TEM image of LaF_3 de-waters.

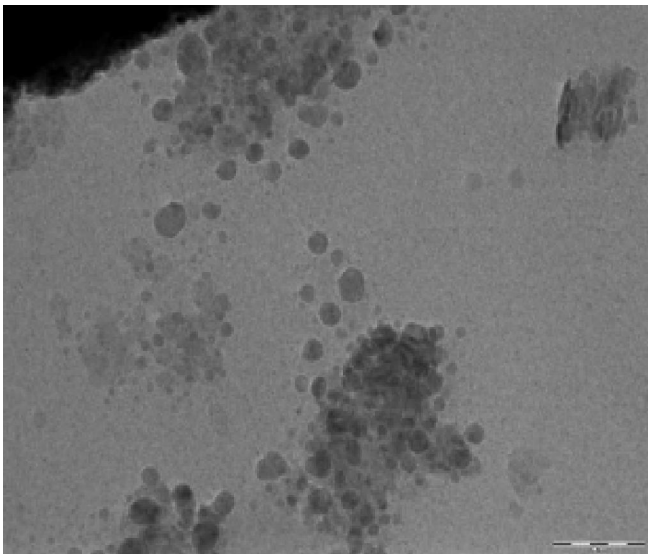

Figure 3(b) : TEM image of LaF_3 methanol

Full Paper

superfine powder synthesized using ethanol as dispersant are very regular. The diameter is in the range of 10-20nm. The cause of this difference may be the hydroxyl of H_2O molecules has higher reactivity than the hydroxyl of C_2H_5OH molecule and is attracted by cations more easily. The hydroxyl of H_2O molecules will become directional and readjust able. 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].

Figure 3(a) and (b) shows the nature and exact dimensions of the synthesized powder was analysed using a TEM (Philips, CM 200, operating voltage: 20-200kv, resolution: 2.4A°). The dispersion medium used was ethyl alcohol. Figure 3 shows a bright field image of LaF_3. The dispersed particles may be due to presence of long chain ligands on the surface preventing aggregation. The average crystalline size of the nanocrystals was well under 10-20 nm. Under high resolution, most nanocrystals formed exhibit well defined crystalline.

Comparison of microwave heating method with traditional preparation methods.

The traditional preparation methods of LaF_3 powder are listed as below:

$$La_2O_3 + 6HF \rightarrow 2LaF_3 + 3H_2O \quad (1)$$

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

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

$$LaCl_3.7H_2O + 3NH_4F \rightarrow LaF_3 + 3NH_4Cl + 7H_2O \quad (4)$$

In reactions (1) and (2), HF is reactant. The SEM image of LaF_3 powder prepared by reaction (4) is shown in Figure 5 As seen from Figure 5, LaF_3 powder is all strip particles, whose average granularity is 10-20 nm.

In reaction (3), there is poisonous HF giving off. This reaction should be heated in alloy tube and kept at 300^0C 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.

CONCLUSIONS

- LaF_3 superfine powder was synthesized from $LaCl_3.7H_2O$ and NH_4F by microwave heating method, using methanol or pure water as dispersant respectively.
- The results of XRD, SEM, and TEM indicate that LaF_3 superfine powder has high purity, regular particle shape, and narrow distribution of granularity. Methanol as dispersant has a great impact on LaF_3 grain size and microstructure. The XRD pattern of LaF_3 powder the in Figure 1 shows that the peak positions and intensities agree well with the data reported in the JCPDS standard card (32-0483) of pure hexagonal LaF_3 crystals. The sizes of the powder were calculated from the XRD pattern based on the Debye–Scherrer formula assuming that the particles are spherical in shape. Figure 3 shows the TEM image of the LaF_3 powder. As can be seen, the nanocrystals have a roughly spherical shape and a particle size 10-20 nm. Which is close to that measured using XRD.
- 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-disturbed granularity of resultant.

REFERENCE

[1] Wang Chang Zhen; Metallurgical Industry Press, (in Chinese), 588-593 **(2000)**.
[2] S.Kuwata, N.Miura, N.Yamazoe; Chemistry Letter, **30**,1295-1299 **(1984)**.
[3] J.M.Dum, H.E.Aldrof, E.C.Barbum; NLGI Spokesman, **48**, 111-116 **(1984)**.
[4] B.P.Sobolev, K.B.Seiranian, L.S.Garashina; Solid State Chemistry, **28**, 51-57 **(1979)**.
[5] B.P.Sobolev, K.B.Seiranian; Solid State Chemistry, **39**, 337-342 **(1981)**.
[6] Jin Qirr han; Microwave Chemistry, **(2001)**.
[7] Tan Tiarren, Mai Berrxi, Ding Hurhua; Chemical Industry Press, 339-347 **(1990)**.
[8] J.Z.Chen; Higher Education Press, 55-63 **(2001)**.