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Synthesis of nano-sized lanthanum oxyfluoride powders by mechanochemical processing

Jaeryeong Lee, Qiwu Zhang*, Fumio Saito

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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Abstract

Lanthanum oxide (La_2O_3) was subjected to grinding with polytetrafluoroethylene (PTFE, $(CF_2CF_2)_n$) in air using a planetary mill followed by thermal treatment to synthesize lanthanum oxyfluoride ultra-fine particles. The grinding operation causes mechanochemical (MC) reaction between the two materials. The MC reaction is almost finished by 240 min, and the products ground for 240 min or more are composed of LaOF, amorphous $La(CO_3)F$ and amorphous carbon (C). Heating this MC reaction product at 600 °C enables us to eliminate amorphous C and decompose $La(CO_3)F$ into LaOF, so that pure LaOF material can be obtained as the final product. The average particle size of the final product (purified LaOF) is around 10 nm.

Keywords: PTFE; Mechanochemical reaction; Lanthanum oxyfluoride with nano-structure; Purification

1. Introduction

Lanthanum oxyfluoride, LaOF, is known to be an activator, a host material of phosphors, a catalyst for oxidative coupling of methane and/or oxidative dehydrogenation of ethane [1–5]. This material has been synthesized by mainly two processes: one is a solid-state synthesis process under high temperature and pressure, causing direct reaction among starting materials [6–10], the other is an electro-winning process, which needs pretreatment for preparing an aqueous solution or a molten salt [11]. In these synthesis methods, lanthanum fluoride or ammonium fluoride has been used as a fluoride source, so that the cost is very high. A more economical method for synthesizing LaOF ultra-fine particles would be strongly expected in the allied industries. The authors have proposed a novel and alternative method for synthesizing particulate functional materials from their constituent mixture without heating [12–15]. This method uses only an intensive grinding-machine such as a planetary mill, so that it is an environmentally friendly method due to no emission of any harmful substances such as fluorine-related gases [16–19]. In addition, this method has the potential to utilize wastes such as a fluorine resin waste instead of lanthanum fluoride or ammonium fluoride. The product synthesized by MC method would contain a greater quantity of impurities than that synthesized by solid-state high temperature reaction. The impurities result from wearing of pot and balls due to intensive grinding. In this research, the authors used a zirconia pot and balls, which are very stable against wearing, in order to limit the contamination considerably.

The main purpose of this paper is to provide information on synthesis of LaOF ultra-fine particles from La_2O_3 and PTFE by mechanochemical (MC) reaction and subsequently thermal treatment.

2. Experimental

Analytical grade lanthanum oxide (La_2O_3, Wako Pure Chemical Industries, Japan) and polytetrafluoroethylene with guaranteed purity (PTFE, $[-CF_2CF_2-]_n$, molecular weight (M_w)=5000–20 000; n, polymerization degree) were chosen as starting materials. Two starting materials were mixed at equivalent molar ratio of F to La, and the mixture was kept in a desiccator. A planetary mill (Pulverisette-7, Fritsch, Germany) was used for grinding the mixture. The mill is composed of a pair of pots made

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*Corresponding author. Tel./fax: +81-22-217-5137.

E-mail addresses: jrlee@iamp.tohoku.ac.jp (J. Lee), zhangqw@tagen.tohoku.ac.jp (Q. Zhang), saito@tagen.tohoku.ac.jp (F. Saito).

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of zirconia installed on a rotating disc being driven by an electric motor. Four grams of the mixture were put in the zirconia pot (45 cm^3 inner volume) with seven zirconia balls of 15 mm diameter. The mixture was subjected to grinding in air at 700 rev./min for various periods of time. Thermal treatment of the ground samples was conducted at about 600 °C for 2 h with two objects: one is to analyze quantitatively the free PTFE content (W) in the ground sample, and using this analysis data we calculated the MC reactivity ($Y = 1 - W$). The other is to purify LaOF fine particles in the ground sample. The details of the quantitative analysis of W are as follows: during thermal treatment (600 °C, 2 h), F_2 gas was generated from the free PTFE in the ground sample, subsequently it was collected completely by absorbing with sodium hydroxide (NaOH, 0.2 N) solution, forming NaF and H_2O. During these operations, the reactions as a monomer unit reaction for the polymer are

$$[CF_2CF_2](s) \xrightarrow{600\ ^\circ C\ \text{in air}} 2F_2(g) + 2CO_2(g) \quad (1)$$

$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(l) + O_2(g) \quad (2)$$

$$4HF(l) + 4NaOH(l) \rightarrow 4NaF(l) + 4H_2O(l) \quad (3)$$

F^- ion concentration in the NaOH solution was measured by an ion chromatograph (IC) (LC10 series, Shimadzu, Japan) to calculate the content of free PTFE in the ground product.

The ground and heated products were characterized by the following methods: an X-ray diffraction (XRD) analysis (RAD-B, Rigaku, Japan) using Cu Kα radiation was conducted to identify the phases formed in the product. An X-ray photoelectron spectroscopic (XPS) analysis (PHI 5600 ESCA system, Ulvac-Phi., Japan) was performed to obtain information on the chemical bonds of materials in the ground product. Infrared spectra of the samples were also measured using an FT-IR spectrometer (Bio-RAD, FTS-40A) with the KBr disc method. Thermogravimetric (TG) analysis was carried out for the ground product using a TG/DTA analyzer (TAS-200, Rigaku) at 5 K/min in air. Morphology and microstructure of the ground and heated products were observed using a high-resolution transmission electron microscope with selected area diffraction (SAD) (JEM-ARM1250, JEOL, Japan).

3. Results and discussion

Fig. 1 shows XRD patterns of the PTFE–La_2O_3 mixtures ground for different periods of time. Peaks of the two materials (La_2O_3 and $La(OH)_3$) are observed in the XRD pattern of the mixture ground for 30 min. The formation of $La(OH)_3$ is due to hydration of La_2O_3 by its adsorption of moisture from the environment, as given by $La_2O_3 + 3H_2O \rightarrow 2La(OH)_3$. This implies that the mechanochemical (MC) reaction has not been achieved yet until 30 min. However, these peaks of La_2O_3 and $La(OH)_3$ decrease gradually and disappear by 120 min. Instead of this change, new peaks appear in the patterns of the mixtures

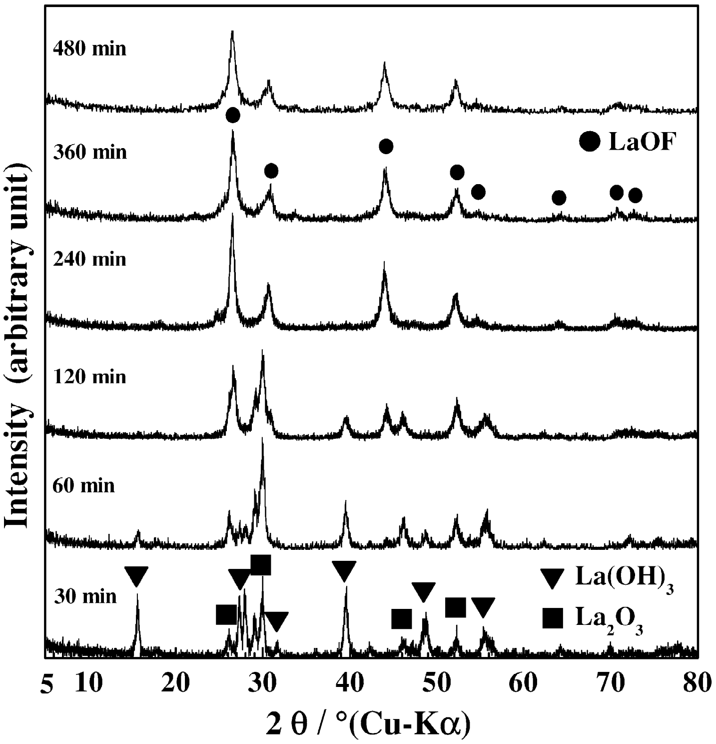


Fig. 1. XRD patterns of the La_2O_3–PTFE mixture ground for different periods of time.

ground for 120 min or more, and their intensities increase as the grinding progresses. They are consistent with the peaks of LaOF (tetragonal, JCPDS no. 5-0470), and only peaks of LaOF are observed in the patterns of the products ground for 240 min or more, entailing that LaOF can be synthesized by grinding for 240 min or more. Of course, the ground products are not only LaOF and they contain other materials at this stage. In addition, the color of the ground products had changed from white to black progressively with an increase in grinding time, suggesting the formation of carbon. This will be discussed in the following XPS analysis.

Fig. 2 shows TG curves of the mixtures ground for different periods of time. These curves can be categorized into two groups; one is a group of short grinding period and the other is a prolonged ground group. As for the former group, significant weight loss in the mixtures can be seen in the temperature range from 300 to 450 °C, reaching about 10 wt.%, irrespective of grinding time. The weight loss is due to the thermal decomposition of mainly PTFE in the mixture, forming F_2 and CO_2 gases. In addition, the initiation temperature in the weight loss is slightly shifted towards the lower side with increase of the grinding time. This means that the polymerization degree of the PTFE decreases due to cutting of the chain as the grinding proceeds. On the other hand, the weight loss of the mixtures in the latter group is observed in the temperature range from about 400 to 500 °C, but the final values are about 8 wt.%, which is smaller than that (10 wt.%) of the former group. Moreover, the initiation temperature in the weight loss is marginally higher by about 100 °C than that for the former group. This suggests that the products and thermally decomposed materials of the mixtures ground for 240 min or more are different from those of the mixtures ground for 120 min or less. Generally, the compounds synthesized mechanochemically have structural defects more or less, which would influence the XRD analysis of them. In these cases, in order to detect even the minor compounds using an XRD analyzer, it is necessary to improve the crystal quality, and annealing of the ground mixture at relatively low temperature is conducted. In this research, annealing was conducted at 300 °C for 2 h. The XRD patterns of the annealed samples are shown in Fig. 3. Only the peaks of LaOF exist in the XRD pattern of the mixture ground for 120 min while new peaks, besides the peaks of LaOF, were observed weakly in the XRD patterns of the mixtures ground for 240 min or more, although they cannot be found in Fig. 1. These new peaks are consistent with those of $La(CO_3)F$ (Hexagonal, JCPDS no. 41-595). It is unexpected that $La(CO_3)F$ can be synthesized at such a low temperature as 300 °C. Therefore, this result indicates that the structural defects of $La(CO_3)F$ were made better by thermal treatment at 300 °C, and the XRD peaks can be observed. That is, the mixtures ground for 240 min or more have included LaOF and $La(CO_3)F$ synthesized by grinding, not by thermal treatment. To confirm these results, FT-IR analysis has been conducted on the following three samples; 480-min-ground product and the products heated at 300 and 600 °C, respectively for 2 h, and the results are shown in Fig. 4. The color of samples has changed gradually from black to white with the increase of temperature. Although it is difficult to identify the peaks in the ground mixture, as for the pattern of the ground mixture heated at 300 °C, the three main peaks are clearly observed: the peak at around 1490 cm^{-1} corresponds to

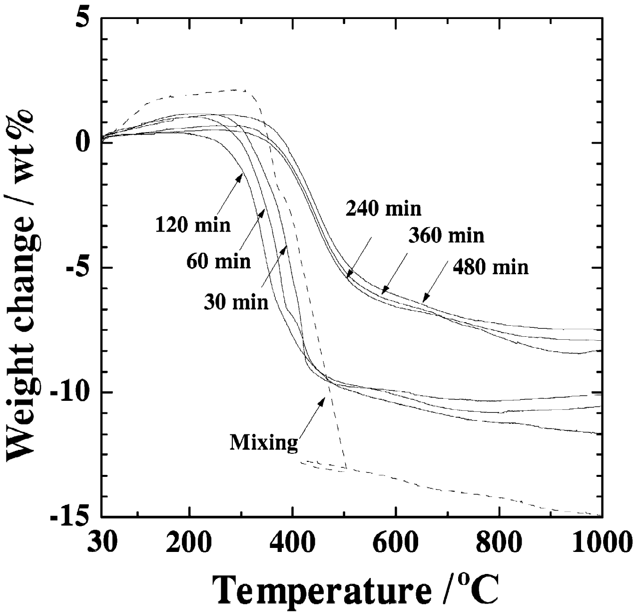


Fig. 2. TG curves of the La_2O_3–PTFE mixture ground for different periods of time.

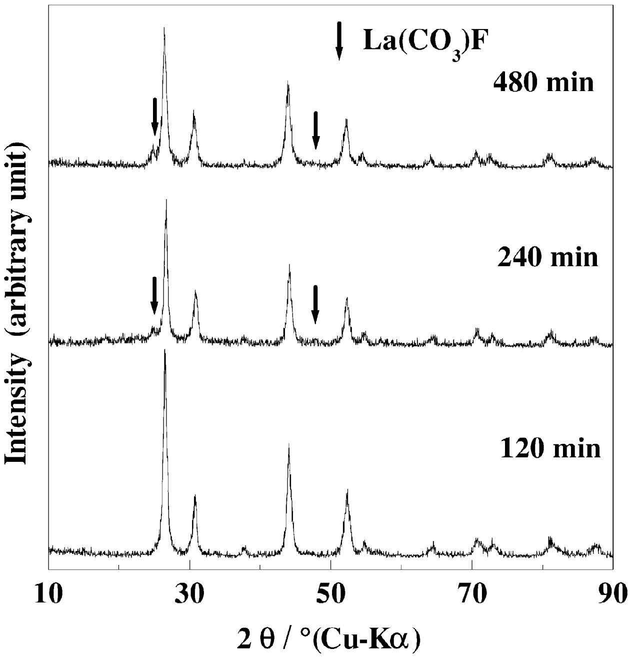


Fig. 3. XRD patterns of the heated mixtures after grinding for different periods of time (T = 300 °C for 2 h).

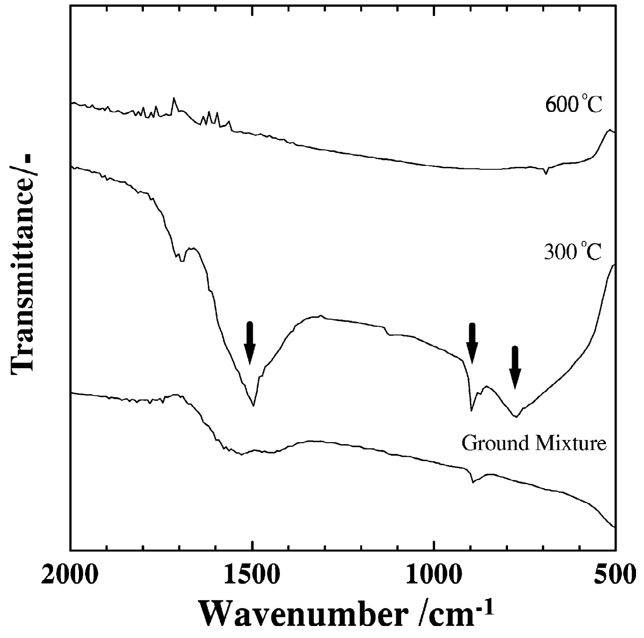
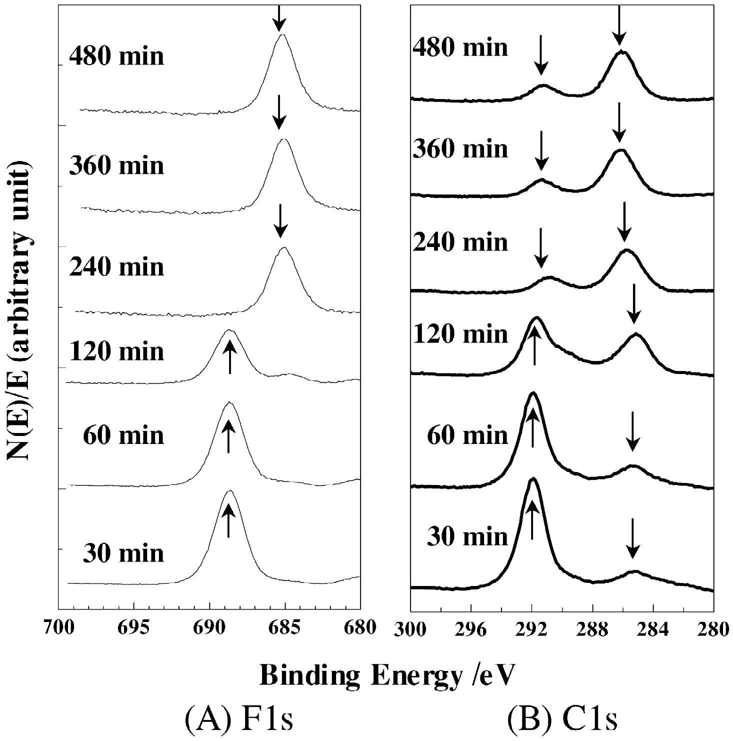


Fig. 4. FT-IR spectra of the 480-min-ground mixture heated at 300 and 600 °C for 2 h.

the C–O stretch, the peaks at 880 cm^{-1} and 740 cm^{-1} correspond to C–O out-of-plane bend and C–O in-plane-bend, respectively. This result indicates the existence of inorganic carbonate and agrees well with the result shown in Fig. 3. There are no significant peaks in the pattern of the product heated at 600 °C, indicating that the inorganic carbonate can be decomposed by heating at 600 °C. Therefore, the weight loss of the latter group in Fig. 2 is due to the decarbonation of $La(CO_3)F$ and the combustion of C.

Fig. 5A and B show XPS spectra on F1s and C1s of the products ground for different periods of time, respectively. Peak intensity at about 689 eV in the spectra shown in Fig. 5A due to the existence of C–F bond decreases with an increase in grinding time, and disappears at 240 min. This implies that defluorination of PTFE has been achieved as the grinding proceeds. Instead of this change, a new peak appears at about 685 eV in the patterns of the mixtures ground for 120 min or more, and its intensity increases gradually as the grinding progresses. About 3.5 eV in energy difference between the two peaks are seen in F1s, suggesting that the fluoride-binding state in the product has been transformed from covalent to ionic bonds [20]. The ionic bond formed is attributed to the formation of LaOF in the ground product, and this is consistent with the results shown in Fig. 1. As for the C1s spectra, two peaks are observed due to the presence of C–F binding at 291±0.5 eV and C–C binding at 285±0.5 eV, respectively. The peak positioned at 291±0.5 eV tends to decrease gradually as the grinding progresses and ultimately disappear by about 240 min of grinding. On the contrary, the new peak at 290±0.5 eV caused by the presence of C–O binding, is observed in the pattern of 120-min ground mixture and this peak increases gradually as grinding proceeds. The peak at 285±0.5 eV increases continuously with an increase of grinding time. In other words, two



(A) F1s (B) C1s

Fig. 5. XPS spectra of the mixture ground for different periods of time.

peaks at 290±0.5 eV and 285±0.5 eV are observed in the patterns of the mixtures ground for 240 min or more and they increase gradually with an increase in grinding time, implying that C–O and C–C bonds have been formed in the product, respectively [21–24]. These bonds are due to the existence of carbonate and carbon, as described earlier. Thus, the mechanochemical reaction between PTFE and La_2O_3 occurred to form LaOF, $La(CO_3)F$ and C. Therefore, the MC reaction between La_2O_3 and PTFE during the grinding can be expressed by Eq. (4), as a monomer unit reaction for the polymer, and the decomposition by thermal treatment at 600 °C in the mixture ground for 240 min or more can be expressed by Eqs. (5) and (6).

Grinding for 240 min or more:

$$2La_2O_3(s) + [CF_2CF_2](s) \rightarrow 3LaOF(s) + La(CO_3)F(s) + C(s) \tag{4}$$

Thermal treatment at 600 °C for 2 h:

$$La(CO_3)F(s) \rightarrow LaOF(s) + CO_2(g) \tag{5}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \tag{6}$$

Fig. 6 shows the MC reactivity as a function of grinding time. The reactivity increases slightly in the early stage of grinding, and reaches about 0.4 at 120 min, then it increases rapidly, reaching about 0.99 at 240 min. Subsequently, the yield tends to increase with leveling off and approaching 1.0 at 360 min. This implies that MC reaction to synthesize LaOF would be accomplished nearly by 240 min and it is completely finished by prolonged grinding for 360 min or over.

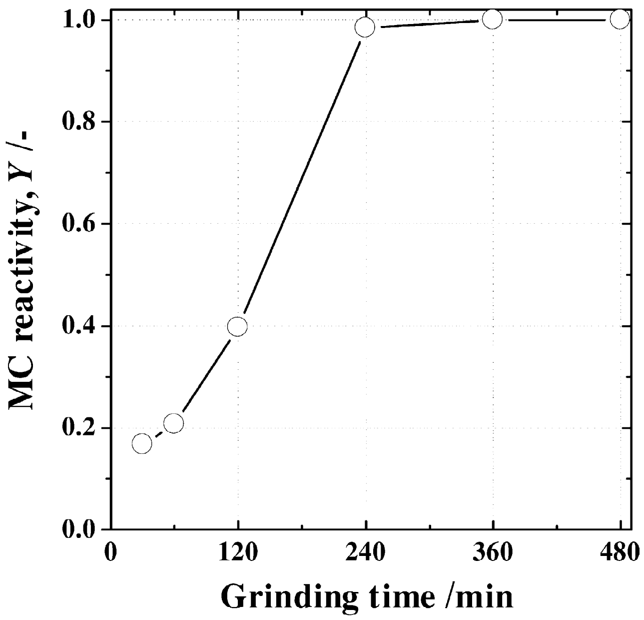


Fig. 6. Reactivity of mechanochemical reaction in PTFE to form LaOF as a function of grinding periods of time.

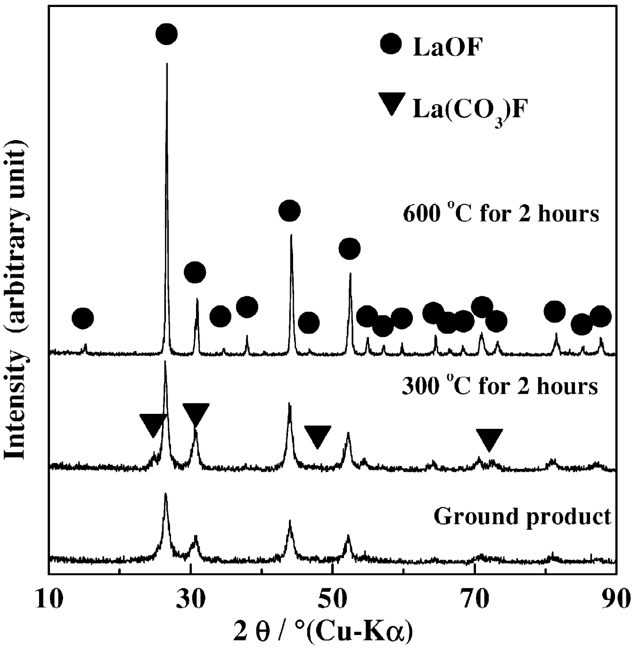


Fig. 7. XRD patterns of the 480-min-ground mixture, and that heated at 300 and 600 °C, respectively.

Fig. 7 shows XRD patterns of the 480-min-ground sample, and that heated at 300 and 600 °C, respectively, for 2 h. The heating at 300 °C makes it possible to improve the crystallinity of $La(CO_3)F$ formed in the product, and the heating at 600 °C enables us to purify LaOF, with decomposition from $La(CO_3)F$ to LaOF and from C to CO_2 in the mixture ground for 240 min or more, as given by Eqs. (5) and (6), as well as with improvement of crystallinity in LaOF.

Fig. 8A–C shows a SAD pattern of the mixture ground for 480 min, its TEM dark field image, and a TEM photograph of the product heated at 600 °C for 2 h. The interplanar spacing calculated by ring pattern in SAD is consistent with that of LaOF (Tetragonal, JCPDS no. 5-0470). The TEM dark field image of the grinding product indicates crystalline fine particles of LaOF, dispersing in amorphous phase, and their first order particle sizes are confirmed to be a few nanometres. The amorphous phase in the TEM image is regarded as amorphous carbon and amorphous $La(CO_3)F$. As shown in the TEM photo of the 480-min-ground mixture heated at 600 °C for 2 h, Fig. 8C, LaOF fine particles with good crystallinity are obtained and their size is about 10 nm.

4. Conclusions

Grinding the mixture of PTFE and La_2O_3 in air by planetary mill was conducted to synthesize LaOF and subsequently thermal treatment at 600 °C was carried out to purify LaOF in the mixture ground for 240 min or more.

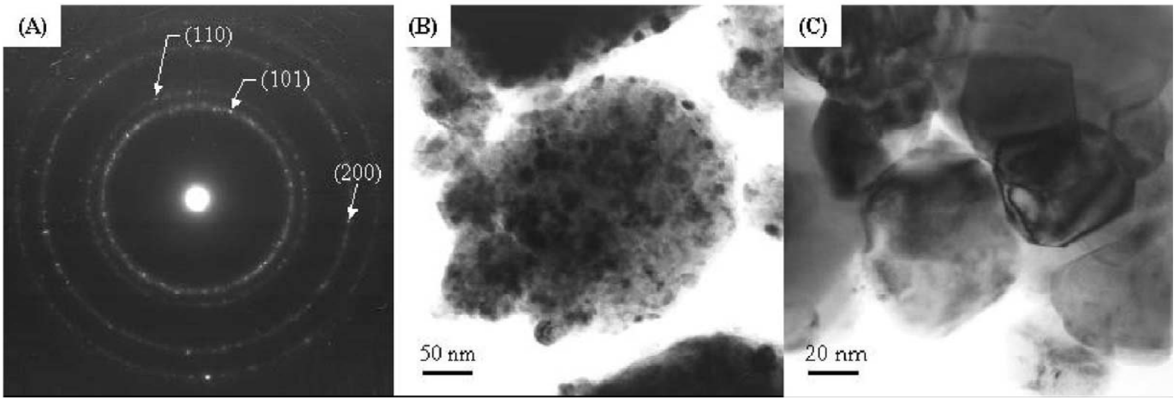


Fig. 8. SAD pattern and typical TEM dark field images. (A) SAD pattern of the 480-min-ground mixture, (B) TEM dark field image of the 480-min-ground mixture, (C) TEM image of the 480-min-ground mixture heated at 600 °C for 2 h.

The following conclusions can be made based on the experimental results.

1. LaOF can be synthesized mechanochemically by grinding of the mixture, and the reaction proceeds with an increase in grinding time. The reaction is almost completed by grinding for about 240 min.
2. The prolonged ground product consists of LaOF, amorphous $La(CO_3)F$ and amorphous carbon and LaOF synthesized mechanochemically is dispersed in the amorphous phases.
3. Thermal treatment at about 600 °C for the mixture ground for 240 min or more enables us to purify the fine particles of LaOF with good crystallinity, without emission of fluorine-related gases. The particle sizes of LaOF purified are about 10 nm.

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