

# Synthesis of lanthanum oxyfluoride by grinding lanthanum oxide with poly (tetrafluoroethylene)

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**Abstract:** Lanthanum oxyfluoride can be synthesized by mechanochemical (MC) reaction between lanthanum oxide ( $\text{La}_2\text{O}_3$ ) and polytetrafluoroethylene (PTFE,  $(\text{CF}_2\text{CF}_2)_n$ ) in air using a planetary mill. MC reaction between the two materials induced from intensive grinding operation. The MC reaction is almost finished by 240min, and the products ground for 240min or more are composed of LaOF, amorphous  $\text{La}(\text{CO}_3)\text{F}$  and amorphous carbon (C). Heating this MC reaction products at  $600^\circ\text{C}$  enables us to eliminate amorphous C and decompose  $\text{La}(\text{CO}_3)\text{F}$  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 few ten nanometers.

## 1. Introduction

Although syntheses and applications of solid fluorides have remained relatively restricted, many future developments can be predicted in certain fields (e.g. related to optical, electrical, and energetic properties) based on such specific features as low refractive index, high ionic conductivity, and low boiling or melting points. Among the fluoride materials, especially lanthanum oxyfluoride, LaOF, is one of the functional materials used as an activator or a host material of phosphors, catalyst for oxidative coupling of methane and oxidative dehydrogenation of ethane and so on. It has been synthesized mainly by direct solid-state and electro-winning processes. The former process requires high temperature and pressure under severe gaseous condition, and the latter needs pre-treatment for preparing aqueous solution or molten salt before the synthesis. Normally, lanthanum fluoride or ammonium fluoride has been employed as a fluoride resource, more economical fluoride resource would be, however, expected in the field of lanthanum oxyfluoride production industries. In the meantime, lots of PTFE wastes have been emitted from industries, which deal with electric products as well as PTFE commodities. These wastes are burned out in disposal facilities, but harmful gases such as HF are emitted, so that another proper method for disposing of PTFE wastes has been required. It would be useful for such PTFE wastes to be reused as a fluoride resource in the synthesis of LaOF. However, little attention has been paid on the reuse of PTFE waste.

The main purpose of this paper is to provide basic information on the mechanochemical synthesis of LaOF by grinding a mixture of  $\text{La}_2\text{O}_3$  and PTFE. This investigation also includes a novel method for disposal of PTFE waste as well as its reuse as a fluoride source in the synthesis of lanthanum oxyfluoride.

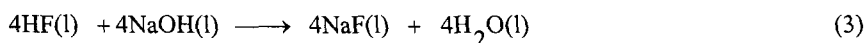
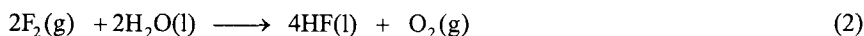
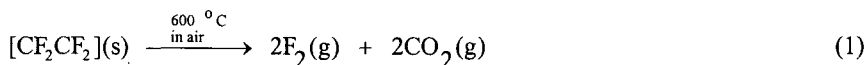
## 2. Experiments

A lanthanum oxide ( $\text{La}_2\text{O}_3$ ), with purity over 99.5 %, and Polytetrafluoroethylene (PTFE,  $[-\text{CF}_2\text{CF}_2-]_n$ , MW 5000-20000), with guaranteed purity, used in the experiment were supplied from Wako pure Chemical Industries, Ltd., Japan. Both samples were mixed at equivalent molar ratio of F to La in the mixture, which was used as a starting sample. A planetary mill (Model Pulverisette-7, Fritsch GmbH, Idar-Oberstein, Germany) was used for grinding the mixture. The mill consists of a pair of pots made of zirconia and rotating disc. Four grams of the mixture was put in the zirconia pot ( $45\text{ cm}^3$  inner volume) with seven zirconia balls of 15 mm diameter and subjected to grinding in air at 700 rpm speed for various periods of time. The ground mixtures were characterized by a X-ray diffraction (XRD) analysis (Model No. RAD-B, Rigaku Co., Ltd., Tokyo, Japan) method using  $\text{Cu-K}\alpha$  radiation to identify the phases formed in the product. X-ray photoelectron spectroscopic (XPS) analysis (PHI 5600 ESCA system, Ulvac-Phi. INC., Chigasaki, Japan) was conducted to obtain the chemical bond information of samples. In the XPS analysis, the X-ray exposure time had been minimized because of decomposition of PTFE by X-ray exposure. Thermogravimetric analysis was conducted by a TG/DTA analyzer (Rigaku Denki, TAS-200) at 5 K/min of heat-

ing rate in air. Morphology and selected area diffraction (SAD) pattern of the ground mixture were observed using a high resolution transmission electron microscope (HREM, JEM-ARM1250, JEOL, Japan).

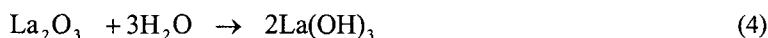
#### As to the quantitative analysis of free (unreacted) PTFE in the ground mixtures

The heat-treating of the ground samples were conducted by about 600 °C for 2 hours. All gases occurring during heat-treating were collected and absorbed successively into sodium hydroxide (NaOH, 0.2 N) solution for three times. The thermal treatment and gas absorption were conducted for leading following reactions, Eq. (1)-(3). F-ion concentrations in solutions were measured by an ion chromatograph (IC) (LC10 series, Shimadzu Co. Ltd.).



### 3. Results and Discussions

Fig. 1 shows the XRD patterns of PTFE and  $\text{La}_2\text{O}_3$  mixtures ground for different periods of time, from 30 to 480 min. In the XRD pattern of mixture ground for 30 min, lanthanum hydroxide was observed as well as lanthanum oxide. Unreacted lanthanum oxide changed to lanthanum hydroxide easily due to adsorption water in atmosphere condition and this change presents as reaction equation, Eq. (4).



Only peaks of the two materials,  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{OH})_3$ , were observed in the pattern of the mixture ground for 30 min, and their peak intensity decreases gradually with an increase of grinding time. On the contrary, new peaks from LaOF appear in the patterns of the mixtures ground for 60 min or more, and its intensity increases as the grinding progresses. In the pattern of the 240 min ground sample, no peaks of the unreacted lanthanum oxide can be observed and all peaks correspond to that of LaOF (Tetragonal, JCPDS No.5-0470). This suggests that LaOF can be synthesized mechanochemically by the grinding, and the reaction can be expressed by Eq. (5), which is showed as a monomer unit reaction. Chemical bonding state of the resultant organic phases will be discussed in the next section from the viewpoint of XPS analysis.

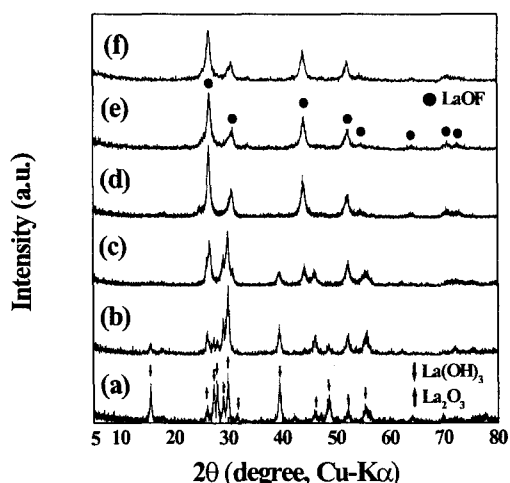


Fig. 1. XRD patterns of the  $\text{La}_2\text{O}_3$  and PTFE mixture ground for different times. (a) 30 min, (b) 60 min, (c) 120 min, (d) 240 min, (e) 360 min, (f) 480 min

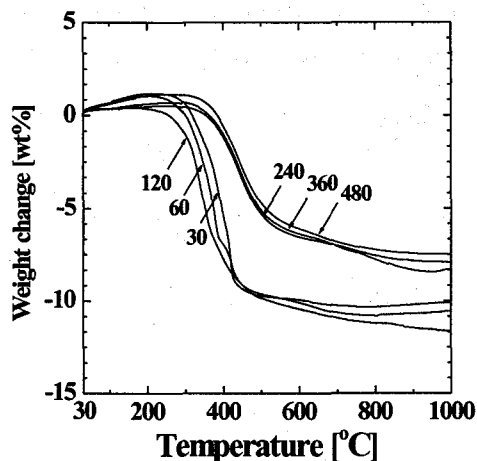
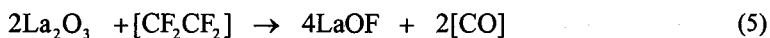


Fig. 2. TG analysis of the  $\text{La}_2\text{O}_3$  and PTFE mixture ground for different times.

Fig. 2 shows the TG curves of the mixtures ground for different periods of time. Significant weight loss of the mixtures can be seen in the temperature range from 300 to 550 °C, due to the thermal decomposition of PTFE in the mixture into  $\text{F}_2$ ,  $\text{CO}_2$  and a like. The weight loss of the mixtures, ground from 30 to 120 min, is measured as around 10 wt%, implying that considerable amount of PTFE remains in the mixture. However, decomposition temperature was taken lower, to say other words, molar weight decreases as the grinding progresses. In the mixture ground for 240 min, the weight loss in range from 300 to 550 °C becomes blunt and reaches to about 8 %. There is no significant difference in the mixture ground over 240 min. This implies that F of PTFE in the mixture is transferred into inorganic phase due to the grinding over 240 min, therefore the weight loss becomes small correspondingly.

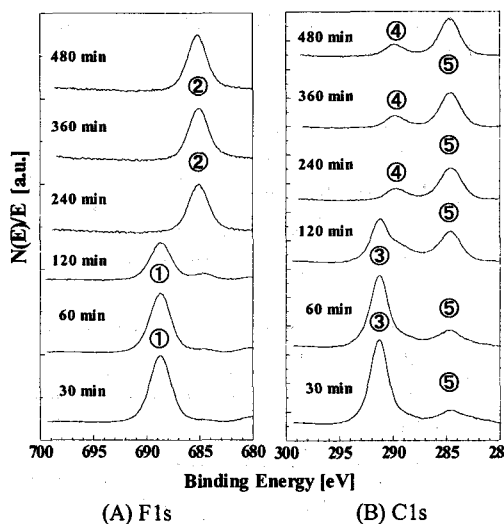


Fig. 3. XPS spectra of the  $\text{La}_2\text{O}_3$  and PTFE mixture ground for different times.

Fig. 3 shows F1s (A) and C1s (B) spectra of the mixture ground for different periods of time. As shown in Fig. 3(A), C-F bond is observed in the spectra. The peak intensity decreases with an increase of grinding time, and dis-

appears at 240 min. This indicates that the C-F bond has been cut off and defluorination of PTFE has been achieved. On the other hand, a new peak appears in the pattern of the mixture ground for 120 min, and its intensity increases gradually as the grinding progresses. About 3.5 eV difference between two peaks can be seen in Fig. 3(A), suggesting that fluoride-binding state has been transformed from covalent to ionic bonds. This ionic bond in the fluoride-binding state is attributed to the formation of LaOF. This is well consistent with the results shown in Figs. 1-2. As for the C1s spectra shown in Fig. 3(B), two peaks due to the PTFE in the mixture imply the existence of CF<sub>2</sub> and C-C bindings at 291 ± 0.5 eV and 285 ± 0.5 eV, respectively. The peak at 291 ± 0.5 eV decreases gradually as the grinding progresses and is disappeared in the mixtures ground for 240 min or more. A new peak of C-O or C=O with peculiar bonding energy, about 290 eV, appears in the pattern of the mixture ground for 120 min and increases gradually with an increase of grinding time. On the contrary, the peak intensity at 285 ± 0.5 eV increases continuously all over the grinding time, ranged from 30 to 480 min.

XRD, TG and XPS results imply that the mechanochemical reaction between PTFE and La<sub>2</sub>O<sub>3</sub> in the mixture takes place through not only degradation of the polymer but also the substitution of F by O from La<sub>2</sub>O<sub>3</sub>. This substitution reaction implies the defluorination of PTFE, and substituted F is used as fluorine resource in the synthesis of LaOF. The resultant organic materials may exist in several different structures, as given by Eq. (6).

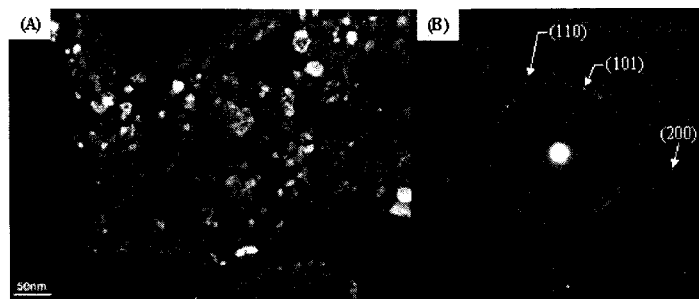
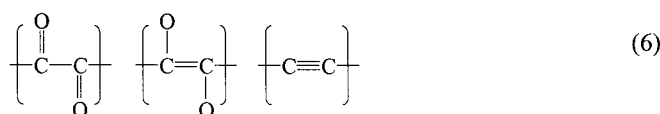


Fig. 4. Typical TEM dark field image (A) and its SAD pattern (B) of the mixture, La<sub>2</sub>O<sub>3</sub> and PTFE, ground for 240 min.

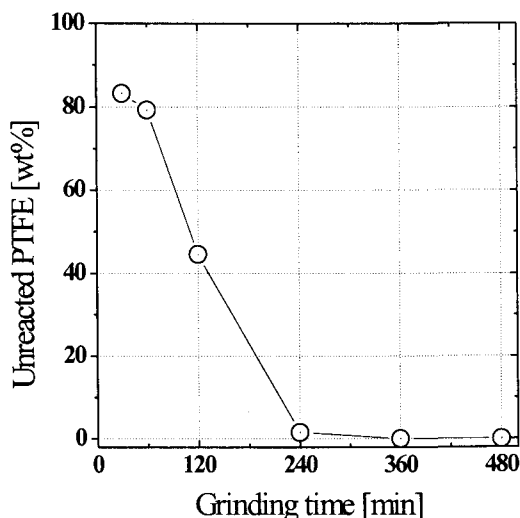


Fig. 5. Percentage of the unreacted PTFE in mixture ground for different times.

Fig. 4 shows (A) TEM dark field image and its (B) SAD pattern of mixture ground for 240 min. This SAD pattern shows the crystalline state of particles. As the results of calculation for interplanar distances using this SAD pattern, they correspond to LaOF's (Tetragonal, JCPDS No. 5-0470) and this result is well consistent with the result shown in Fig. 1. TEM dark field image was achieved using the strongest diffraction plane, (101). As shown in (A), crystal particles are dispersed in amorphous material and their first order size is several nanometers. This result indicates that LaOF nanoparticles are synthesized and they are dispersed in amorphous resultant organic materials during mechanochemical reaction in the  $\text{La}_2\text{O}_3$  and PTFE mixture.

Fig. 5 shows the change in the percentage of PTFE unreacted in the mixtures ground for different periods of time. In the beginning of grinding time, the percentage of PTFE decreases very slowly and reaches about 80 % at 60 min. Subsequently, it decreases more rapidly from 60 min, and reaches about 99 % at 240 min. After all, it reaches to 100 % for 360 or more. This result implies that the purification of LaOF from mixture ground for 360 min or more can be achieved without no fluorine-related gases.

#### 4. Conclusions

The following conclusions can be made based on the experimental results

- (1) LaOF can be synthesized by the room temperature grinding of  $\text{La}_2\text{O}_3$  and PTFE through their solid-state reaction. This reaction through the substitution of F by O results in the defluorination of PTFE, with synthesizing LaOF. After mechanochemical reaction, only LaOF materials can be acquired simply and safely using thermal treatment, about 600 °C for 2 hours. The mechanochemical reaction proceeds with an increase in grinding time and is almost completed by about 240 min.
- (2) The size of the synthesized LaOF powder is several nanometers, and the particles are dispersed in the amorphous resultant organic materials.
- (3) The new bands, such as C-O, C-C, C=C and C≡C, are formed in the resultant organic phase in the ground mixture.

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