

Mechanochemical Synthesis of LaOX ($X = \text{Cl}, \text{Br}$) and Their Solid State Solutions

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A mixture of lanthanum oxide (La_2O_3), chloride (LaCl_3), and bromide (LaBr_3) was ground in air by a planetary ball mill to investigate synthesis of lanthanum oxychloride (LaOCl), oxybromide (LaOBr), and their solid solutions, $\text{LaOCl}_{1-x}\text{Br}_x$ ($0 \leq x \leq 1$, $\Delta x = 0.25$). The synthesizing reactions proceed with an increase in grinding time. Unit cell dimensions, a , c , and lattice volume of the solutions evolve linearly with an increase in x in the $\text{LaOCl}_{1-x}\text{Br}_x$ series. Comparing unit cell dimensions of LaOX synthesized by mechanochemical reaction to those of LaOX synthesized by solid-state reaction at high temperature, there is no difference in the length of c , while a is shortened slightly. This may be attributed to the complex cation layer of $(\text{LaO})_n^+$, with a close relationship to a of the cell dimensions, being affected by the intensive grinding. © 2001 Academic Press

Key Words: LaOCl; LaOBr; mechanochemical reaction; PbFCl structure; lattice parameter deviation.

INTRODUCTION

Lanthanum oxyhalides (LaOX , $X = \text{F}, \text{Cl}, \text{Br}$) have unique and excellent characteristics in electrical, magnetical, optical, and luminescent properties (1–8). Especially the luminescent property is based on the rare earths either as a dopant or as a host which plays an important role in phosphor compounds. Furthermore, the solid solution of the host anions, such as Cl and Br, in the lanthanum oxyhalide lattice should elevate the luminescent properties in phosphor (9–17).

LaOX have been synthesized by two methods, direct solid-state reaction at high temperature and electro-winning method (18–20). Each of them has severe drawbacks in the synthesis process, such as the demand of strict temperature, pressure and atmospheric conditions for the former and the demand of pretreatment and complicated process for the latter, respectively. In spite of these drawbacks in process, the synthesized LaOX materials have several defaults in

homogeneity, size distribution, and so on. Therefore, a new synthesis process that is much simpler and able to synthesize LaOX with excellent physical and chemical properties has been strongly required. The authors have reported that mechanochemical (MC) method allows the synthesis of lanthanum oxyfluoride (LaOF) particles with nanometric sizes by grinding a mixture of La_2O_3 and LaF_3 in air (21). This suggests that the MC synthesis of LaOCl , LaOBr , and their anion solid solution, $\text{LaOCl}_{1-x}\text{Br}_x$, could be achieved by grinding constituent components.

The main purpose of this paper is to provide information on the synthesis of lanthanum oxyhalides by the mechanochemical treatment of $(\text{La}_2\text{O}_3\text{--LaCl}_3)$ or $(\text{La}_2\text{O}_3\text{--LaBr}_3)$ systems.

EXPERIMENTAL

Lanthanum oxide (La_2O_3), lanthanum chloride (LaCl_3), and lanthanum bromide (LaBr_3) were used in the experiment, and their chemical reagents are in the purity of 99.5%. The lanthanum oxide was supplied from Wako Chemical Co., Ltd. (Osaka, Japan), and the lanthanum chloride and bromide from High Purity Chemetals Laboratory Co., Ltd. (Saitama, Japan). The lanthanum oxide was mixed with lanthanum halide (LaX_3 , $X = \text{Cl}$ or Br) at an equimolar ratio of La to X, respectively. As for a starting mixture of anion solid solution, La_2O_3 was mixed with a mixture of LaCl_3 and LaBr_3 , so as to be equal to 1 in total La/X molar ratio. 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 a rotating disc. Four grams of the mixture was put in the zirconia pot (45 cm³ inner volume) with seven zirconia balls of 15 mm diameter and subjected to grinding in air at 700 rpm for various periods of time. The ground products were characterized by X-ray diffraction (XRD) analysis (Model RAD-B, Rigaku Co., Ltd., Tokyo, Japan) method using $\text{CuK}\alpha$ radiation ($\lambda = 1.541838 \text{ \AA}$) to identify the phases formed in the product. Furthermore, the XRD data from 20° to 80° in scattering angle were analyzed with the

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aid of the Rietveld profile method by using the LCR2 program (22). Lattice fringe and selected area diffraction (SAD) pattern of the ground mixture were observed using a high-resolution transmission electron microscope (HREM, JEM-ARM1250, JEOL, Japan).

RESULTS AND DISCUSSION

Mechanochemical Synthesis of LaOX ($X = \text{Cl}, \text{Br}$)

Figure 1 shows XRD patterns of the La_2O_3 and LaBr_3 mixture ground for different periods of time, from 30 to 240 min. LaBr_3 tends to change its crystal structure into the amorphous state easily; therefore no peaks of LaBr_3 are observed in the pattern of the 30-min-ground mixture, shown in Fig. 1a. Peak intensity of La_2O_3 in the mixtures decreases gradually with an increase in grinding time, while new peaks of LaOBr (Tetragonal, JCPDS No. 47-1676) appear in the patterns of the mixtures ground for 60 min or more, and their intensity increases as the grinding progresses. Their increment levels off in the XRD pattern of the mixtures ground for 120 min or more. No other peaks can be observed in the XRD patterns of 120 min or more, suggesting that LaOBr has been synthesized mechanochemically by the grinding of the mixture. The synthesis reaction can be expressed by

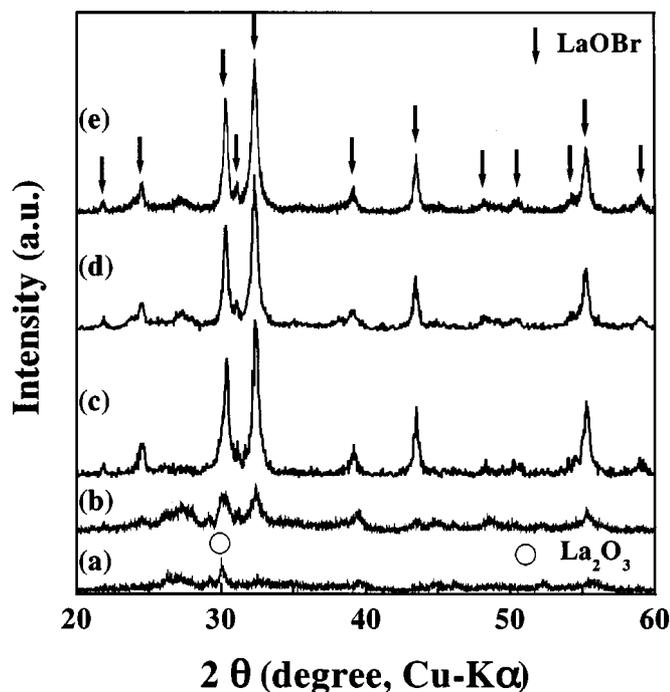


FIG. 1. XRD patterns of the La_2O_3 and LaBr_3 mixture ground for different times: (a) 30 min, (b) 60 min, (c) 120 min, (d) 180 min, (e) 240 min.

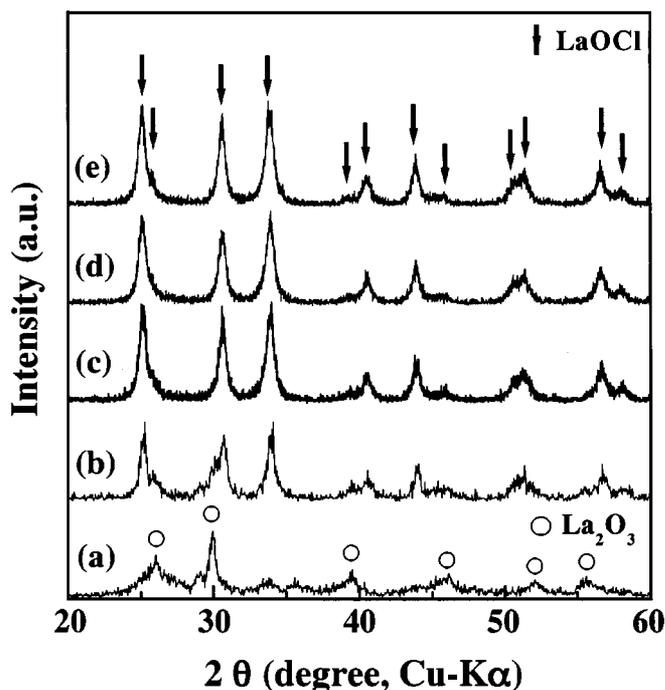


FIG. 2. XRD patterns of the La_2O_3 and LaCl_3 mixture ground for different times: (a) 30 min, (b) 60 min, (c) 120 min, (d) 180 min, (e) 240 min.

Figure 2 shows XRD patterns of the mixture of La_2O_3 and LaCl_3 ground for different periods of time, from 30 to 240 min. Similar to the pattern shown in Fig. 1, LaCl_3 tends to change its crystal structure into the amorphous state easily; therefore, no peaks of LaCl_3 are observed in the pattern of 30 min ground mixture and the oxide peaks decrease gradually with an increase in grinding time in the initial stage of grinding, and they disappear completely in the XRD pattern of the 120-min-ground mixture. On the contrary, new peaks of LaOCl appear in the patterns of the mixtures ground for 60 min or more, and the intensity increases as the grinding progresses. In the pattern of 120-min-ground sample, all peaks correspond to that of LaOCl (Tetragonal, JCPDS No. 34-1494). This result indicates that the MC reaction takes place within 120 min in grinding time, as given by



In Figs. 1 and 2, the change of XRD pattern for grinding over 120 min is imperceptible. This suggests that the crystal structure of LaOCl or LaOBr synthesized mechanochemically is sustained even in prolonged grinding. In addition, both compounds have the same crystal structure, represented by PbFCl structure (Tetragonal- C_{4v} symmetry, $P4/nmm$, $Z = 2$) (23).

Figure 3 shows (a) TEM images, (b) SAD patterns, and (c) HREM images of (A) LaOBr and (B) LaOCl synthesized

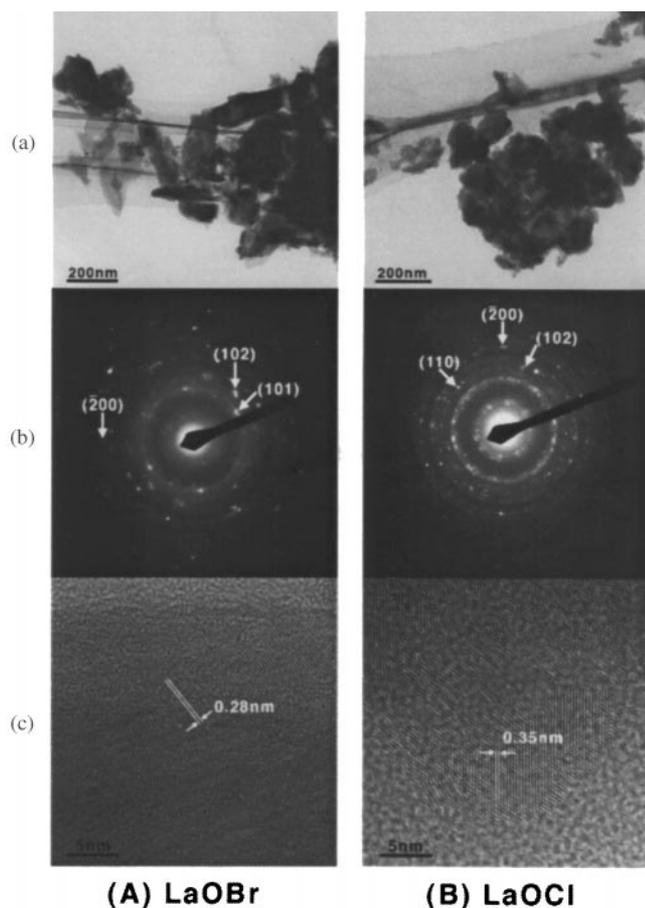


FIG. 3. (a) Typical TEM images, (b) SAD patterns, and (c) HREM images of (A) LaOBr, (B) LaOCl synthesized by grinding for 4 h.

mechanochemically by the grinding for 240 min. As shown in TEM images (a), particles look like agglomerates, but the first-order particle size is on the order of nanometers. As for the case of LaOBr, shown in Fig. 3A(a), the agglomerate consists of particles several hundreds of nanometers size, with wide size distribution. The crystallite size of LaOBr and LaOCl synthesized by grinding for 4 h was calculated by Scherrer's equation based on their diffraction plane, (102). Their crystallite sizes of LaOBr and LaOCl are 19 and 15 nm, respectively. For the LaOCl particles (Fig. 3B(a)), their sizes look like relatively small and the size distribution seems to be narrower than that of LaOBr. In the SAD patterns shown in (b), it is found that the particles in the both compounds synthesized consist of small subunits (sub-crystals) with slight variation in crystal orientation. The diffraction planes of LaOBr and LaOCl were determined by interplanar angles, on the basis of main diffraction planes, (102) and (110), respectively. Regarding the HREM images of LaOBr and LaOCl, shown in (c), the fine fringes corresponding to the crystal lattice of the LaOBr and LaOCl can

be seen clearly on the atomic scale. The interplanar spacings, 0.28 and 0.35 nm, were measured from the lattice planes of LaOBr and LaOCl, respectively.

Mechanochemical Synthesis of Solid State Solution

The achievement of mechanochemical synthesis of LaOCl and LaOBr leads us to the synthesis of $\text{LaOCl}_{1-x}\text{Br}_x$ solid solution. Figure 4 shows XRD patterns of the five kinds of mixture ground for 4 h: the mixture of La_2O_3 , LaBr_3 , and/or LaCl_3 , corresponding to (a) LaOBr, (b) $\text{LaOCl}_{0.75}\text{Br}_{0.25}$, (c) $\text{LaOCl}_{0.5}\text{Br}_{0.5}$, (d) $\text{LaOCl}_{0.25}\text{Br}_{0.75}$, and (e) LaOCl. As shown in Fig. 4, each pattern resembles closely the pure LaOCl or the pure LaOBr diffraction pattern, only a smooth variation of the reflection positions and intensities can be observed; that is, the diffraction angles decrease slightly as the Br^- mole fraction increases, which results from the difference in the ionic radius of the two host anions of LaOCl and LaOBr, with similar structure. No splitting of the reflections or appearance of new reflections can be seen in these patterns, indicating that no intermediate phases in the $\text{LaOCl}_{1-x}\text{Br}_x$ series and no formation of other material besides the solid solutions could be observed. This may be due to two reasons: one is the homogeneity of compounds synthesized by MC reaction, the other is the similar structure of LaOCl to that of LaOBr, as well as the

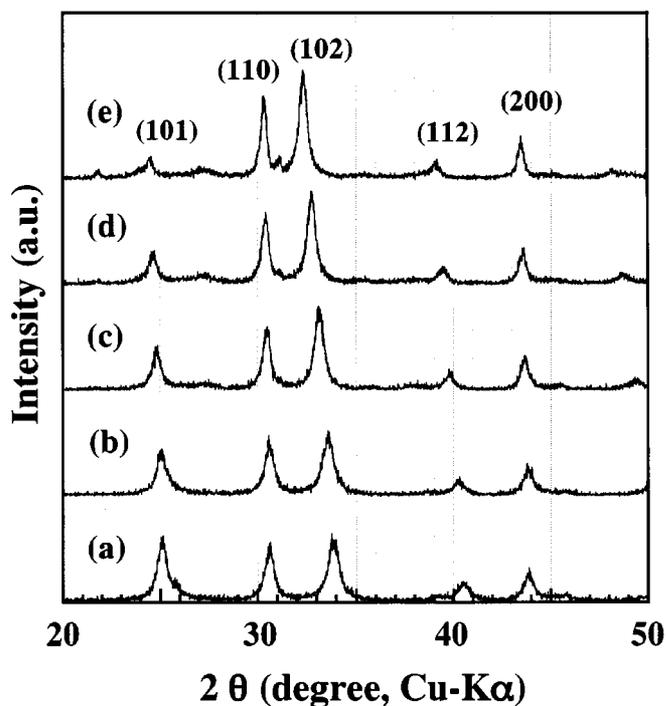


FIG. 4. XRD patterns of the $\text{LaO}(\text{Cl}_{1-x}\text{Br}_x)$ phases ($x =$ (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0).

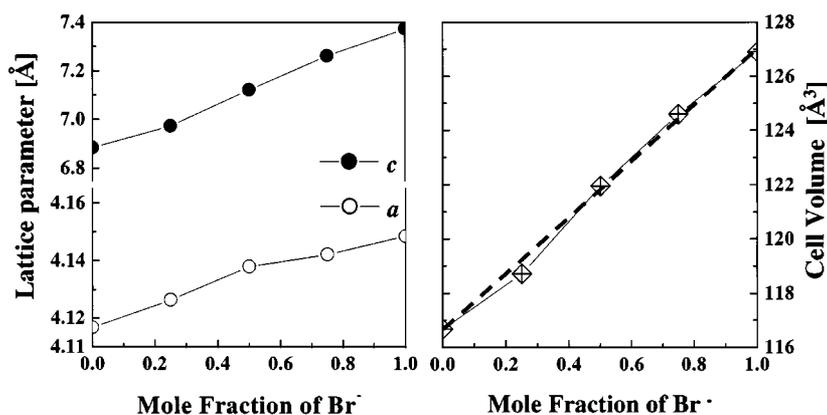
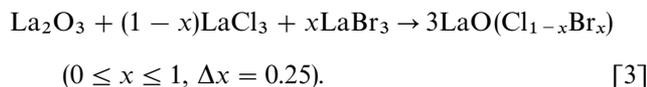


FIG. 5. Evolution of the unit cell parameters in the $\text{LaO}(\text{Cl}_{1-x}\text{Br}_x)$ synthesized by mechanochemical reaction.

small difference in the ionic radius of the two host anions, i.e., 1.81 and 1.96 Å for the Cl^- and Br^- ions, respectively. The mechanochemical reaction forming $\text{LaOCl}_{1-x}\text{Br}_x$ anion solid solution can be given by



In order to provide more information on the structure of the $\text{LaOCl}_{1-x}\text{Br}_x$ system synthesized by MC reaction, we calculated the lattice parameters using the Rietveld method on the basis of XRD data. Figure 5 shows lattice parameters, a , c , and cell volume of the system as a function of mole fraction of Br^- . As shown in Fig. 5, the smooth and practically linear evolution of the unit cell parameters, a and c , indicates complete solid solubility. However, a slight curvature could be observed in the middle of the series, but the cell volume remained constant in this region. The slight deviation of a , in disagreement with Vegard's law (24), may be explained as follows. The indication of anomalies in anion substitution in the $\text{LaOCl}_{1-x}\text{Br}_x$ series is attributed to the atom position parameters for different atoms. Both of the La and Cl atoms occupy a special twofold position $(0, \frac{1}{2}, z)$, whereas the oxygens reside in a rather similar position, $(0, 0, 0)$ (23). Furthermore, comparing unit cell dimensions of LaOX synthesized by the MC method to those of LaOX synthesized by the high-temperature method, there is no difference in the length of c , while a is shortened slightly. That is to say, a in this research is 4.1485 for LaOBr (4.1576 of JCPDS No. 47-1676) and 4.1168 for LaOCl (4.120 of JCPDS No. 8-477). In the field of mechano-synthesis of materials including mechanical alloying, the change of lattice parameters due to grinding has been observed and reported (25–29). The decrease observed in the LaOX systems may be explained based on their lattice structures as follows. In the tetragonal LaOCl and LaOBr with space

group $P4/nmm$ (No. 129, $Z = 2$), their structures comprise distinct covalent $(\text{LaO})_n^{n+}$ complex cation and anion X ($X = \text{Cl}, \text{Br}$) layers perpendicular to the c -axis of the unit cell (30). In these structures, the La^{3+} ion is coordinated to four oxygens and five halides (one on the fourfold axis) forming a monocapped tetragonal antiprism as the coordination polyhedron. The point symmetry of the La^{3+} site is C_{4v} . The La–O distances within the rigid LaO_4 unit vary slightly in the halide series, whereas the La– X distance along the four-axis increases with the size of the halide. That is to say that the $\text{LaOCl}_{1-x}\text{Br}_x$ series have the complex cation layer of $(\text{LaO})_n^{n+}$ and the unit cell dimension a , which is related to this layer, decreases due to intensive grinding (31).

CONCLUSION

The following conclusions can be made based on the experimental results

- (1) LaOBr and LaOCl , with PbFCl (tetragonal- C_{4v} symmetry, $P4/nmm$, $Z = 2$) crystal structure, can be synthesized mechanochemically by the room-temperature grinding of La_2O_3 and LaBr_3 , La_2O_3 , and LaCl_3 , respectively. This mechanochemical reaction proceeds with an increase in grinding time and is almost completed by 120 min. Both LaOCl and LaOBr synthesized sustain their crystal structures in the prolonged grinding.
- (2) The first-order particle sizes of the synthesized LaOBr and LaOCl are in nanometric order, and the particles are in a state of agglomerate.
- (3) $\text{LaOCl}_{1-x}\text{Br}_x$ can be also synthesized by the grinding of a mixture of La_2O_3 , LaCl_3 , and LaBr_3 . The smooth and practically linear evolution of the unit cell parameters, a and c , indicates complete solid solubility, where a is shorter slightly, compared with that of sample prepared by high temperature method.

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