

Rapid communication

Preparation of the cubic-type La_2O_3 phase by thermal decomposition of LaI_3

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Abstract

Cubic lanthanum oxide was prepared by the oxidation of lanthanum iodide at 700 °C in air atmosphere. The oxide was characterized by X-ray fluorescence analysis, X-ray diffraction, and Fourier-transformed infrared spectroscopy. The cubic La_2O_3 is most likely a single lanthanum oxide phase containing periodate hydrate and hydroxycarbonate species. The cubic lanthanum oxide is found to be chemically stable even if they are dispersed in water because of the presence of hydroxycarbonate and periodate hydrate species which inhibit the bulk hydroxylation.

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1. Introduction

Lanthanum oxide (La_2O_3) has a lot of attractive properties for applications such as catalysts [1], high κ gate dielectric material [2] and optical filters [3]. In recent years, study on the preparation and property of chemically stable La_2O_3 has attracted much interest from a practical point of view. Although basic properties of La_2O_3 with hexagonal structure have been investigated [4–8], the chemical stability of La_2O_3 is not sufficient. For example, hexagonal La_2O_3 usually reacts with H_2O and CO_2 to form hydroxide and carbonate species when it is left in air [7–10]. As an alternative candidate, cubic La_2O_3 has been prepared. The cubic La_2O_3 powder is prepared by slow thermal decomposition of lanthanum hydroxide [11] and their films are obtained by chemical vapor deposition of metal organic compounds [2,12]. However, the cubic La_2O_3

films were found to be chemically unstable in an ambient air due to a chemical reaction with moisture to form monoclinic $\text{LaO}(\text{OH})$ [12].

On the contrary, in this communication, we have found that the cubic La_2O_3 can be stabilized if the powder is prepared by the thermal decomposition of the lanthanum iodide. From the viewpoint of the stabilization of lanthanum oxide, the present method is assumed to be beneficial, and, therefore, preparation and characterization of the cubic La_2O_3 are discussed here.

2. Experimental

Lanthanum oxide powder was prepared by a simple calcination of lanthanum iodide (99.9%, High Purity Chemicals, Japan), which was heated at 700 and 900 °C for 12 h in air atmosphere for the preparation of cubic and hexagonal La_2O_3 , respectively. Composition of the samples was analyzed by an X-ray fluorescent (XRF) spectrometer (Rigaku, ZEX-100e). X-ray

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powder diffraction (XRD) data were collected with an X-ray diffractometer (Rigaku, Multiflex) using $\text{CuK}\alpha$ radiation in the 2θ range from 10° to 70° by a step width of 0.04° . Thermal gravimetric and differential thermal analyses (TG-DTA) were carried out (Shimadzu, DTG-60H) using α -alumina as a reference. Fourier-transformed infrared (FT-IR) spectra of the powders were measured with an FT-IR spectrometer (Bruker, TENSOR 27).

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns of the La_2O_3 samples prepared by the calcination of LaI_3 at 700°C (a), 750°C (b), and 900°C (c), respectively. The XRD peaks observed in the sample (a) in Fig. 1 correspond to the (222), (400), (440), (622) and (444) reflections of the cubic La_2O_3 [2,11], while the sample (c) presents the reflections of the hexagonal La_2O_3 . At annealing temperature of 750°C (b), a mixture of both cubic and hexagonal La_2O_3 was obtained.

Stoichiometry and impurity residues of the cubic La_2O_3 at various temperatures were quantitatively determined by XRF. The contents of La, O, I, and C in the cubic La_2O_3 were calculated by the normalization of the relative X-ray intensities of these elements with individual standard values. The atomic composition of the cubic La_2O_3 powder synthesized at 700°C was about 34.8at% La, 54.2at% O, 6.2at% I, and 4.8at% C, respectively. The iodine and carbon contents in the sample are not enough to be LaOI and $\text{La}_2\text{O}_2\text{CO}_3$ phases. Furthermore, neither tetragonal LaOI nor hexagonal $\text{La}_2\text{O}_2\text{CO}_3$ peaks are found in the XRD patterns as depicted in Fig. 1, but only a cubic La_2O_3 is formed in a single phase at this temperature.

The TG-DTA analysis was performed at a heating rate of $10^\circ\text{C min}^{-1}$ to investigate the thermal properties of the cubic La_2O_3 . A broad endothermic peak with gradual weight loss and a sharp endothermic peak accompanying with a rapid weight loss were detected at around 400 and 820°C , respectively, as depicted in Fig. 2, indicating that vaporization occurred at these temperatures. In the references, cubic La_2O_3 phase is reported to change at around 600°C [2,12], while in the present study, the cubic La_2O_3 can exist in a single phase at least up to 700°C . According to the thermogravimetric result, the weight loss ratio of 13.2 wt% from 700 to 900°C is almost equal to the calculated value (13.4 wt%) corresponding to the release of iodine and carbon dioxide. Taking into account of the above results and some references [9,12–13], the first peak in the TG-DTA curve indicates the evolution of water molecule and the second peak represents that of iodine and carbon dioxide [9].

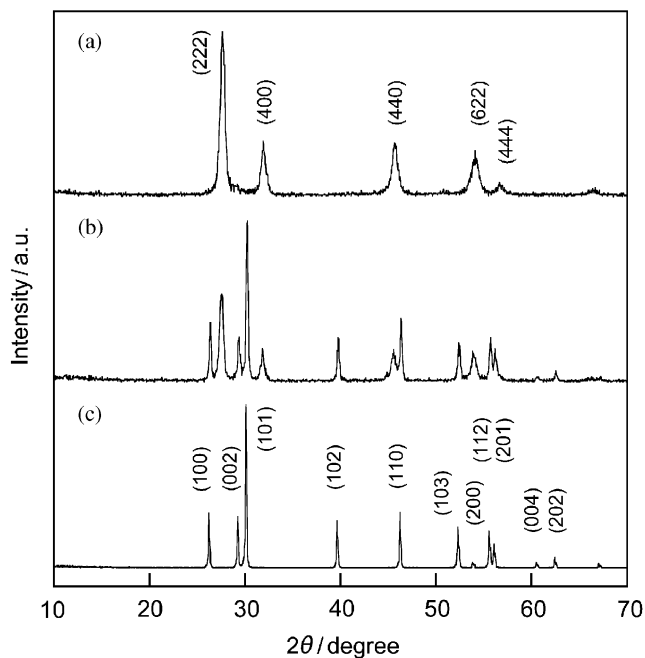


Fig. 1. XRD patterns of La_2O_3 powder prepared at (a) 700°C , (b) 750°C and (c) 900°C by the calcination of LaI_3 for 12 h in atmospheric air.

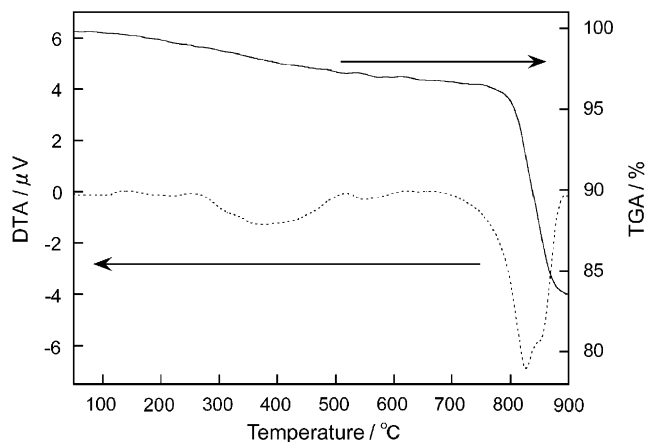


Fig. 2. TG-DTA diagram of the cubic La_2O_3 powder.

FT-IR spectra of the cubic and the hexagonal La_2O_3 samples synthesized at different temperatures were measured immediately after the sample preparation in order to discuss structural and chemical information in detail (Fig. 3). The spectrum of the cubic La_2O_3 consisted of infrared absorption bands at 422, 654, 849, 1157, 1410, 1508, 1637, 2343, 2361 and 3448 cm^{-1} . Strong peaks around 422 and 654 cm^{-1} observed in the spectrum can be indexed as being due to the stretching mode of the La–O and the deformation mode of La–OH, respectively [9,14]. The bands at 849 and 1157 cm^{-1} are attributed to I–O stretching and I–O–H bending modes, respectively [15,16]. Two weak bands at 2343 and 2361 cm^{-1} also come from deformation of

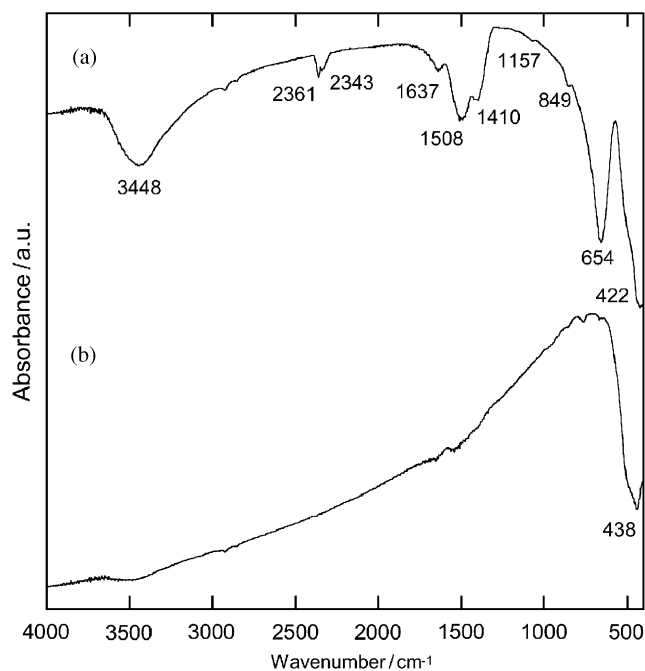


Fig. 3. FT-IR spectra of (a) cubic La_2O_3 synthesized at 700°C and (b) hexagonal La_2O_3 synthesized at 900°C .

I–O–H mode involving bridging hydrogen [15,16]. These results indicate that the iodine exists as periodate hydrate species.

On the other hand, the bands at 1410 and 1508 cm^{-1} are carbonate species absorbed from the atmosphere, and similarly, the broad band at 3448 cm^{-1} is due to the stretching mode of water [9]. The FT-IR results suggest that carbon is mainly present as a hydroxycarbonate in the sample. The presence of the 1637 cm^{-1} band due to the H–O–H bending mode indicates water as distinct from –OH species, suggesting the existence of both hydroxide ions and molecular water in the cubic La_2O_3 [9,17]. These bands were eliminated by the increase of calcination temperature which is consistent with the decrease of iodine (not detectable) and carbon (1.1 at%) contents in the hexagonal La_2O_3 prepared at 900°C , as found in Fig. 3(b). Therefore, it is considered that the cubic La_2O_3 prepared in the present study is most likely a single lanthanum oxide phase containing periodate hydrate and hydroxycarbonate species, because no peak other than the cubic phase was observed in the XRD pattern as discussed above.

The chemical stability of the cubic La_2O_3 was also investigated. It has been reported that the intensity of the XRD reflection of cubic La_2O_3 decreases and that of monoclinic $\text{LaO}(\text{OH})$ phase appears when a cubic La_2O_3 film is stored in a desiccator for a few days, because the cubic La_2O_3 film absorbs water from ambient air to induce partial transformation to lanthanum oxide hydroxide easily [12]. In contrast, the cubic La_2O_3 presented in this study is much chemically stable.

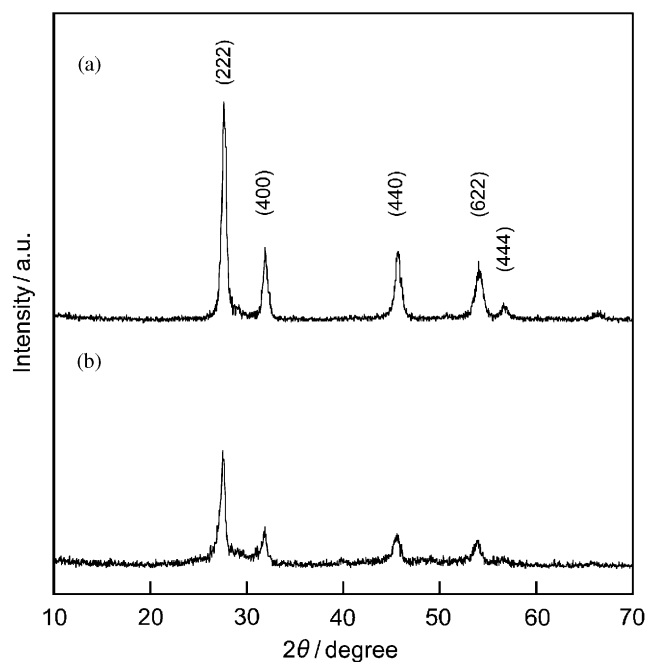


Fig. 4. XRD patterns of the cubic La_2O_3 powders (a) before and (b) after dispersion in water for 2 h.

XRD patterns of the present cubic La_2O_3 samples before and after dispersion in water for 2 h are illustrated in Fig. 4. The sample was dispersed in water using magnetic stirrer for 2 h. Although no ultrasonic procedure was used, the particles were well-dispersed with vigorous stirring. The formation of $\text{LaO}(\text{OH})$, $\text{La}(\text{OH})_3$, La_2O_2 , CO_3 and $\text{La}_2(\text{CO}_3)_3$ phases was not observed in the XRD pattern after the treatment, although the crystallinity of the sample slightly decreased.

The chemical composition of the sample unchanged after washing, which indicates the chemical stability of the cubic La_2O_3 . Although it has not been clear yet as to why and how the presence of hydroxycarbonate and periodate hydrate species inhibit the hydroxylation of the particles, the presence of these phases critically affects the stabilization of cubic La_2O_3 phase, considering the facts that (i) the carbonation process is limited to the outer layer of La_2O_3 [9,10], because the apparent thermal stabilization of the oxide is attained when the carbonation level is relatively low [9], (ii) the FT-IR results suggest that the iodide exists as peroxide hydrate species (Fig. 3a), and (iii) the cubic La_2O_3 containing only oxycarbonate or hydroxycarbonate species is unstable, while the cubic La_2O_3 presented in this study is chemically stable even if it is washed with water. Since the peak widths in Fig. 4(b) did not change after washing, the decrease of the intensity of the peaks in the diffraction pattern was probably due to the loss of crystallinity by the partial transformation of the cubic phase to an amorphous phase that was difficult to be clearly detected by XRD measurement.

In conclusion, it has been shown that cubic La_2O_3 can be synthesized by a simple calcination of LaI_3 at 700°C in air atmosphere. The structural and chemical analyses of the cubic La_2O_3 suggest that iodine, carbon, and hydroxyls could be responsible for the stabilization of the cubic phase. Moreover, in contrast to the previous materials reported, the cubic La_2O_3 presented in this study is chemically stable even if it has been dispersed in water for 2 h.

Acknowledgments

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