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Preparation of apatite-type $La_{9.33}(SiO_4)_6O_2$ oxide ion conductor by alcoxide-hydrolysis

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Abstract

Both powder and film of apatite-type $La_{9.33}(SiO_4)_6O_2$ were prepared by alcoxide-hydrolysis. The apatite formation temperature was considerably lowered in this preparation method comparing to its solid-state reaction. Its sintered body did not show any particular orientation of the anisotropic apatite crystals. Electrical conductivity was 7.2×10^{-5} S cm^{-1} at 500 °C. The films deposited on quartz glass and Pt substrates with thickness of either 1.0 or 1.5 μm had uniform microstructure extended on their surface. Preferred orientation of $La_{9.33}(SiO_4)_6O_2$ was observed on the surface of the film deposited on quartz glass substrate; its basal plane was parallel to the substrate.

Keywords: Oxide ionic conduction; Sol–gel synthesis; Rare earth silicate; Thin film

1. Introduction

Oxide ion conductors are important in their application to sensors, solid oxide fuel cells and oxygen pumps. Rare earth silicates with the apatite-type structure ($RE_{9.33}(SiO_4)_6O_2$; RE = La–Dy) were recently reported as new oxide ion conductors [1,2]. They showed an appreciably higher conductivity than that of stabilized zirconia at relatively low temperatures below 600 °C. The highest electrical conductivity reported was 4.3×10^{-3} S cm^{-1} at 500 °C on its sintered body. The apatite has been prepared by solid-state reaction between La_2O_3 and SiO_2 in high temperature above 1600 °C [1,2]. Either La_2SiO_5 or $La_2Si_2O_7$ is easily formed as an impurity. Once they appear, it is difficult to remove by further firing. Homogeneous mixing of the starting materials can be more easily attained in solution process, e.g. sol–gel synthesis using metal alcoxides than in solid-state reaction.

Bulk single crystals were grown by floating zone method for $Pr_{9.33}(SiO_4)_6O_2$, $Nd_{9.33}(SiO_4)_6O_2$ and $Sm_{9.33}(SiO_4)_6O_2$ [3–5]. Their electrical conductivities were very anisotropic because of the conduction channel along *c*-axis. The value parallel to hexagonal *c*-axis was larger in about one order of magnitude than that perpendicular to *c*-axis. Large anisotropic displacement parameters were observed on oxide ions in the channel by single crystal X-ray and neutron powder diffractions [6–9]. Its crystal orientation should be controlled in polycrystalline solids to achieve its real application for oxide ion conductor. Its film formation has not been studied except for phosphor application [10–12]. Tao and Irvine have reported the $La_{9.33}(SiO_4)_6O_2$ powder synthesis by the sol–gel method [13], but there has been no research on oxide ion conductive film. Crystal orientation has not yet been studied on its sintered body. Change of powder morphology may have some effect on the orientation effect.

In this study, $La_{9.33}(SiO_4)_6O_2$ was prepared by hydrolysis of alcoxides. Its crystalline orientation was studied both on its thin film and sintered body in relation to electrical conductivity.

2. Experimental procedure

La_2O_3 and TEOS were used as the starting materials. Lanthanum oxide (1.11 g) was dissolved in 5 ml of 6 M HNO_3 and mixed with 10 ml of ethanol. Then, stoichiometric amount of

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TEOS (1.00 ml, i.e. La:Si = 9.33:6) in ethanol of 20 ml was added to this solution. Precursor solution was obtained by refluxing for one night. This solution was heated to gelating on the hot plate in powder preparation, followed by calcination and annealing.

Either quartz glass or Pt foil substrate was dipped to the gelatinous solution and dried for the film preparation. It was calcined at 500 °C for 1 h to remove the organic contents, and then fired at 1000 °C for 10 h. This preparation steps were repeated to increase the film thickness.

The microstructure was observed by scanning electron microscopy (JEOL, JSK-6300F). X-ray diffractometer (PHILIPS, X'pert-MPD) with monochromatized Cu Kα was used for phase identification and crystalline orientation measurement. Powder sample for the electrical measurement was uniaxially pressed into a pellet and sintered at 1400 °C for 10 h. Both sides of the pellet were then coated with Pt paste as electrodes. The electrical conductivity was measured using AC impedance meters (YHP 4274A (0.1–100 kHz) and HP 4285A (0.1–1 MHz), respectively).

3. Results and discussion

3.1. $La_{9.33}(SiO_4)_6O_2$ powder

XRD patterns of $La_{9.33}(SiO_4)_6O_2$ powder obtained at different firing conditions are shown in Fig. 1. Product was essentially amorphous after calcination at 500 °C for 1 h. Either La_2O_3 or La_2SiO_5 appeared when the sample was calcined at 600 °C. They could not react to give $La_{9.33}(SiO_4)_6O_2$, even if the sample was fired again at a temperature above 1000 °C. The apatite-type lanthanum silicate was obtained with a small amount of La_2O_3 and La_2SiO_5 impurities when the sample was annealed at 1000 °C for 10 h (Fig. 1a). Well-crystallized apatite was obtained by annealing at 1400 °C for 10 h (Fig. 1b) as reported in Ref. [13]. This firing temperature is lower than 1600 °C required to obtain pure $La_{9.33}(SiO_4)_6O_2$ in solid-state reaction [1,2]. The apatite was formed at considerably lower preparation temperature in this preparation method. SEM observation showed that the powder was sintered hexagonal platy crystals as shown in Fig. 2a. The hexagonal habit can be related to the apatite structure with hexagonal crystal lattice. There was no obvious preferred orientation in its X-ray diffraction pattern. The sintering of the primary particles should be solved to obtain preferred orientation. Surface of the sintered body did not show any particular sign of preferred orientation in XRD (Fig. 1c) and SEM (Fig. 2b).

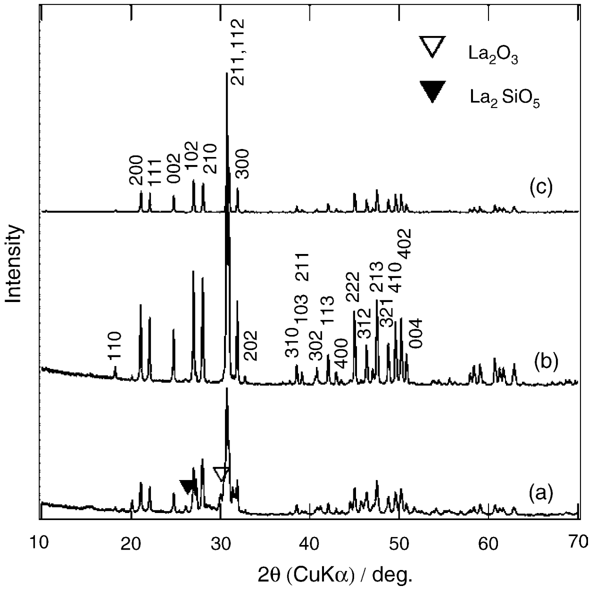

Fig. 1. XRD patterns of $La_{9.33}(SiO_4)_6O_2$: (a) powder sample annealed at 1000 °C for 10 h, (b) 1400 °C for 10 h and (c) surface of sintered body.

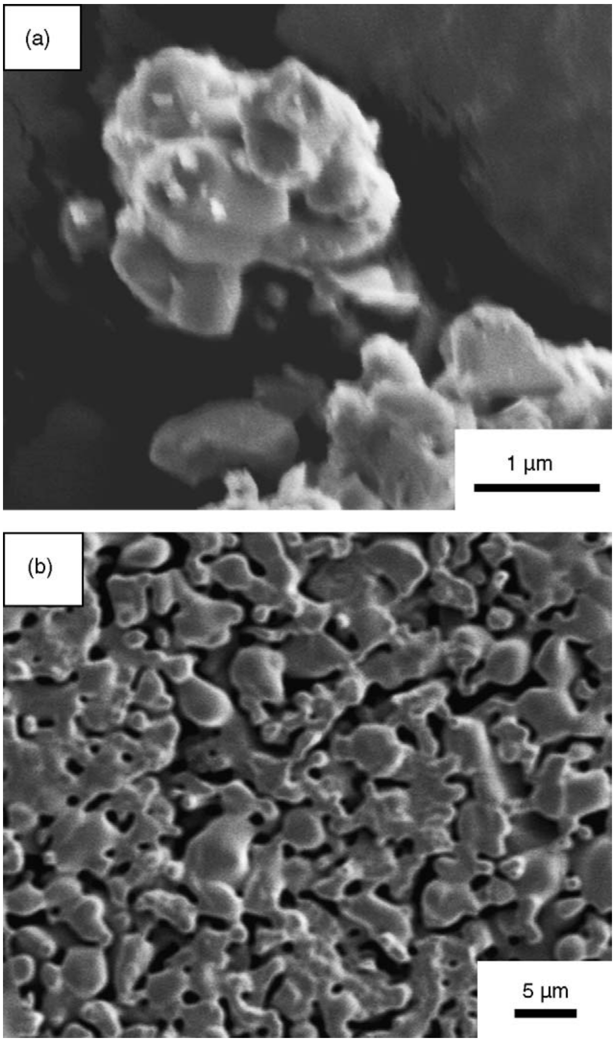

Fig. 2. SEM image of $La_{9.33}(SiO_4)_6O_2$ powder annealed at 1400 °C for 10 h (a) and sintered body surface (b).

3.2. $La_{9.33}(SiO_4)_6O_2$ film

The film formed on quartz glass substrate was amorphous when it was calcined at 500 °C. The apatite phase appeared

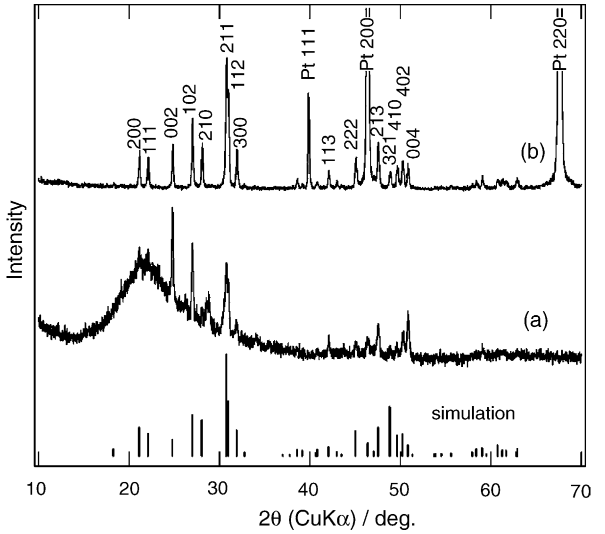

Fig. 3. XRD patterns of $La_{9.33}(SiO_4)_6O_2$ films on (a) quartz glass and (b) Pt foil substrates. The films were prepared by annealing at 1000 °C for 10 h after calcination at 500 °C for 1 h. Diffraction lines simulated using the data from Ref. [8] are shown at the bottom.

after its successive annealing at 1000 °C for 10 h as shown in Fig. 3a. Preferred orientation of the apatite crystals was observed comparing the observed data with the simulated pattern for non-oriented $La_{9.33}(SiO_4)_6O_2$ using structure data obtained in single crystal structure analysis [8]. The diffraction lines of 0 0 2 and 0 0 4 were emphasized against those of 2 1 0 and 4 1 0. SEM observation showed uniform microstructure of 1.0 μm thick extended on its surface. The film reacted with quartz glass substrate to form amorphous interface layer. Pt paste electrode fired on the film surface for electrical measurement easily peeled off at the interface amorphous layer.

The film was formed on Pt sheet as non-reactive substrate. Apatite phase appeared after annealing at 1000 °C in a similar way of using the quartz glass substrate (Fig. 3b). The relative intensity of 0 0 2 and 0 0 4 diffractions was almost the same with the simulated pattern. The film was thicker in this case than the above-mentioned film because wetting between the alcoxide gel and substrate was poorer than the previous case. SEM observation showed that particles of about 100 nm diameter sintered each other forming uniform porous film surface of 1.5 μm thick as shown in Fig. 4. Preferred orientation of the apatite crystals was not so obvious as in the film formed on quartz glass substrate, because apatite crystals precipitated in the thicker film.

3.3. Electrical conductivity

AC electrical conductivity for the $La_{9.33}(SiO_4)_6O_2$ sintered body changed against temperature as shown in Fig. 5. Its bulk and grain boundary contributions could not be resolved in the semicircles of cole–cole plots. The electrical conductivity reported here represents the total conductivity. The conductivities were $7.2 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$ at 500 °C and $1.4 \times 10^{-3}\ \mathrm{S\,cm^{-1}}$ at 800 °C and changed in Arrhenius' equation. They were almost comparable with polycrystalline sample prepared by solid-state reaction as shown in Fig. 5. They were compared with the conductivities of $Nd_{9.33}(SiO_4)_6O_2$ single crystal in Fig. 5, because $La_{9.33}(SiO_4)_6O_2$ single crystal have not yet been grown in floating zone method. Bulk single crystals had been grown for praseodymium, neodymium and samarium silicates. Electrical conductivities were almost the same independently on the kinds of rare earth element [5]. The present electrical conductivity of $La_{9.33}(SiO_4)_6O_2$ sintered body was lower about one order of magnitude than that of perpendicular to *c*-axis for the $Nd_{9.33}(SiO_4)_6O_2$ single crystal. The anisotropic oxide ion conduction was averaged in the sintered body without particular orientation. The conductivity was lower than the value perpendicular to *c*-axis. The sintered body had a relative density of about 80% having a lot of pores in its matrix. Non-conductive impurities of La_2SiO_5 or $La_2Si_2O_7$ were also observed in its grain boundary. The film formed on quartz glass substrate peeled off when Pt paste electrode was fired on its surface. The film prepared on Pt foil was very porous. Pt paste was infiltrated into the porous matrix. Further trials are required to make good electrodes on the apatite films.

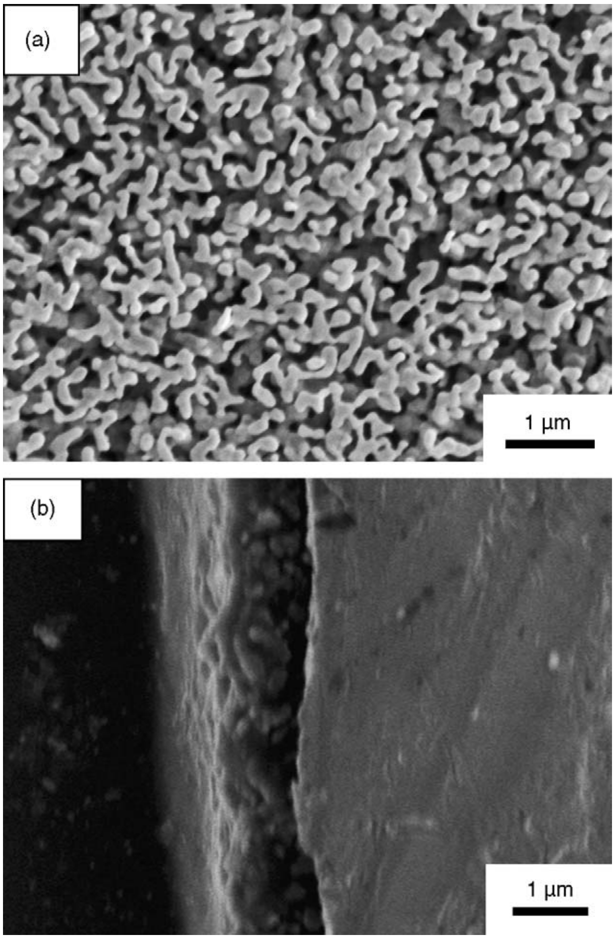

Fig. 4. SEM images of $La_{9.33}(SiO_4)_6O_2$ film on Pt substrate (a) surface and (b) its cross-section.

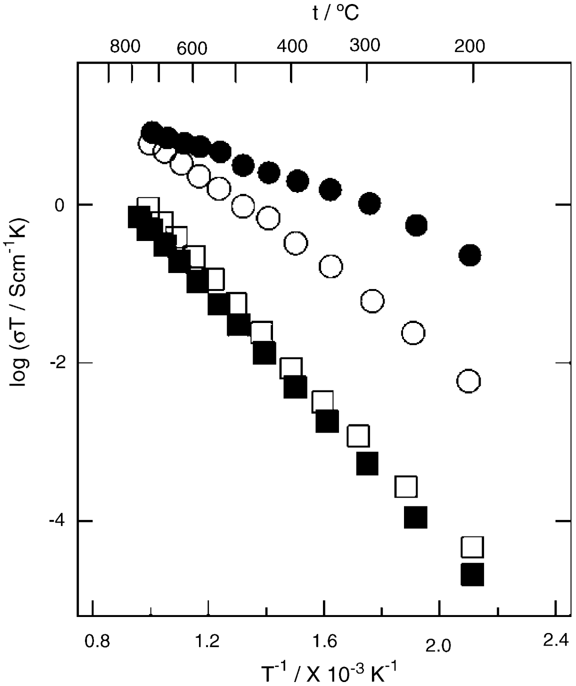

Fig. 5. Temperature dependence of electrical conductivities. Symbols (□ and ■) represent the values for polycrystalline $La_{9.33}(SiO_4)_6O_2$ prepared by present method and solid-state reaction, respectively. Symbols (● and ○) correspond to those for $Nd_{9.33}(SiO_4)_6O_2$ single crystal along and perpendicular to *c*-axis [3], respectively.

4. Conclusions

Apatite-type lanthanum silicate powder and film were prepared by alcoxide-hydrolysis using lanthanum nitrate solution and TEOS. Apatite phase was formed at the relatively low temperature of 1000 °C comparing to a conventional solid-state reaction. The film showed preferred orientation of the apatite crystal in thinner film. The conductivity of sintered body was lower in about one order of magnitude than the value perpendicular to *c*-axis of single crystal.

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