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Electrical conductivity and X-ray diffraction analysis of oxyapatite-type lanthanum silicate and neodymium silicate solid solution

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ABSTRACT

In this study, we determined the crystallographic nature and electrical transport properties of $Nd_{9.20}(SiO_4)_6O_{1.8}$ and $(La_{0.46}Nd_{0.54})_{9.33}(SiO_4)_6O_2$, which are defect-containing oxyapatites. The intensity data measured by synchrotron powder X-ray diffraction were analyzed by a Rietveld method. From the total conductivity data, the oxygen partial pressure region where the oxygen ionic conductivity ($\sigma_{O^{2-}}$) predominates was determined to narrow down owing to the substitution of neodymium ions. A comparison of various solid solutions under similar temperature conditions ranging from 873 K to 1273 K showed that the $\sigma_{O^{2-}}$ values were lowest for $(La_{0.46}Nd_{0.54})_{9.33}(SiO_4)_6O_2$ samples. The activation energy of the oxygen ionic conductivity increased with an increasing neodymium content.

1. Introduction

Since the discovery of high oxygen ionic conductivity in lanthanoid silicate oxyapatites by Nakayama et al., several researchers have been interested in determining the relationship between the oxygen ion conductivity and crystal structure [1–8]. Being a unique feature of the oxyapatite family, this oxygen ion conductivity shows a crystallographic anisotropy confirmed by conductivity measurements performed on single crystals of neodymium silicate, praseodymium silicate, and samarium silicate [4]. Moreover, the oxygen ionic conductivity values are found to strongly depend on the lanthanoid ion species in the ceramic samples [1–4].

The general chemical composition of lanthanoid silicate oxyapatites is given as $Ln_{9.33+\alpha}(SiO_4)_6O_{2+3\alpha/2}$ (where *Ln* is lanthanoid ions with trivalence). The electrical transport properties of $Ln_{9.33}(SiO_4)_6O_2$, which corresponds to the oxygen stoichiometric composition, are of great significance because they are a function of the oxygen partial pressure; a study of these properties aids in determining the width of the oxygen partial pressure region with anti-Frenkel defects predominance. However, detail research exist related to the oxygen partial pressure dependence on conductivity of $Ln_{9.33}(SiO_4)_6O_2$ due to the difficulty of synthesizing single-phase $Ln_{9.33}(SiO_4)_6O_2$. The amount of oxygen ions related to the oxygen ionic conduction is considered to be influenced by the value of α. It is very difficult to synthesize single-phase oxyapatite with different α compositions below 1773 K without using another dopant species. However, we previously succeeded in synthesizing a single-phase ceramic samples of lanthanum silicate oxyapatite with a $La_{9.50}(SiO_4)_6O_{2.25}$ composition by a water-based sol–gel method [9]. Neodymium silicate oxyapatite with lower neodymium concentrations has been reported to be obtained by a conventional solid-state reaction method between 1673 K and 1873 K [10,11] and a water-based sol–gel method followed by a heating step at 1773 K [12]. In particular, by the use of the water-based sol–gel method, neodymium silicate oxyapatite single-phase crystals with a composition of $Nd_{9.20}(SiO_4)_6O_{1.8}$ could be synthesized by heating at 1773 K [12]. Through a combination of these techniques, i.e., via a water-based sol–gel method employed with a solid-solution mixture of pseudo-binary $La_{9.50}(SiO_4)_6O_{2.25}$ and $Nd_{9.20}(SiO_4)_6O_{1.8}$, samples with various oxygen ion contents can be synthesized. However, data on the crystallographic and electrical transport details of such lanthanum silicate and neodymium silicate oxyapatite solid solutions have not yet been reported. Values of the cell parameters and total conductivity recorded at 773 K and 1073 K for $(La_{0.97}Nd_{0.03})_{9.66}(SiO_4)_6O_{2.49}$ synthesized at 2023 K have, however, been measured [13]. Nevertheless, crystallographic details of $La_{9.50}(SiO_4)_6O_{2.25}$–$Nd_{9.20}(SiO_4)_6O_{1.8}$ solid solutions have not been reported before.

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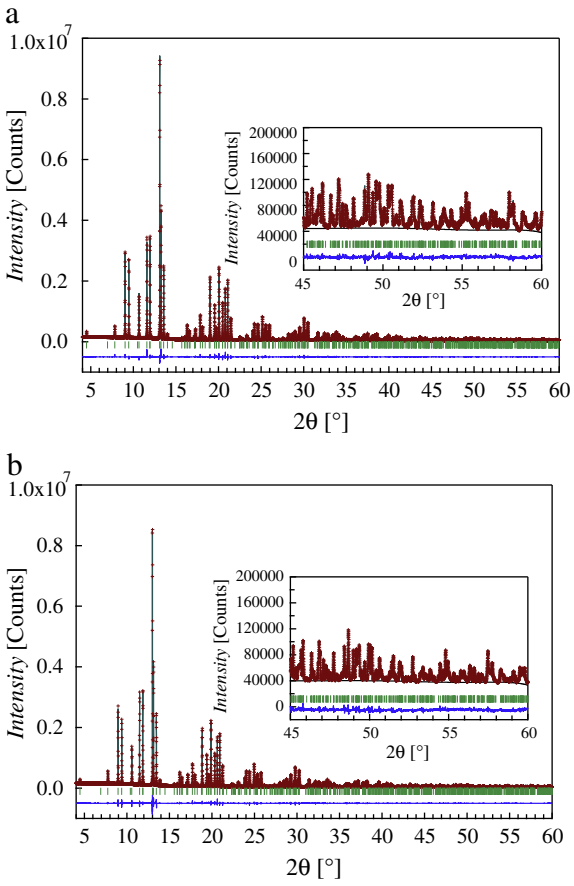

Fig. 1. Synchrotron powder X-ray diffraction profiles and results of Rietvelt analysis of (a) Sample B and (b) Sample C. The plotted fitted curves, peak position, and residual curves were calculated by RIETAN-FP [14]. Inset shows a blow-up profile at high 2θ region.

In this study, we synthesized oxyapatite solid solutions of lanthanum silicate and neodymium silicate with oxygen stoichiometric composition by applying a water-based sol–gel method. The mixing effect of La and Nd on the crystallographic natures and the electrical transport properties were investigated by synchrotron powder X-ray diffraction analysis and conductivity measurements.

2. Experimental

All of the samples used in this study, with nominal compositions; $La_{9.50}(SiO_4)_6O_{2.25}$ (sample A), $Nd_{9.2}(SiO_4)_6O_{1.8}$ (sample B), and $(La_{0.46}Nd_{0.54})_{9.33}(SiO_4)_6O_2$ (sample C), were synthesized by a previously reported water-based sol–gel method [9]. The precursor powders were preheated at 1273 K for 3 h in air and subsequently pressed into pellets under 63 MPa. The pellets were sintered at 1773 K for 24 h in air. Average grain size of the sintered ceramic samples was approximately 5 μm by scanning electron microscopy (SEM) observation. Some of the sintered pellets were crushed into powders that were used for the X-ray diffraction (XRD) analysis using a laboratory X-ray diffraction instrument (JDX-3500, JEOL Co., Japan). To determine the crystallographic details of sample B and sample C, they were examined by synchrotron powder X-ray diffraction technique at BL15XU, SPring-8 (Japan). Finely powdered samples were packed into capillaries (Lindenmann glass, 0.2 mm diameter), and the diffraction data at 295 K were collected at a wavelength of 0.065297 nm. The structural parameters were refined by a Rietveld analysis performed with RIETAN-FP [14]. On the Rietveld analysis of sample B and sample C, we applied stoichiometric models for both compounds, because the models gave more realistic results. The anistropic atomic displacement refinements were also carried out to all sites, except at the O1, O2, and O3 sites of $Nd_{9.20}(SiO_4)_6O_{1.8}$ and the O2 site of sample C. These exceptions were made because it was found that the fitted parameter values of the above sites obtained using the anisotropic atomic displacement parameters were experimentally inadequate. Therefore, an isotropic atomic displacement parameter was used for these sites. The bond length and bond angle were calculated using the crystallographic software VESTA [15].

The total conductivity was measured as a function of oxygen partial pressure and temperature following a two-probe ac-method implemented using an impedance analyzer (NF 5090, NF Co., Japan) with frequency ranging from 1 MHz to 0.1 Hz. Platinum electrodes were attached to both samples by painting them with platinum paste and subsequently firing them at 1273 K for 30 min in air. The temperature range for the conductivity measurements was varied between 873 K and 1273 K. The oxygen partial pressure of the sample environment was varied from 1 atm to 10^{-25} atm using $Ar+O_2$ and $Ar+H_2+H_2O$ gas mixtures. The oxygen partial pressure of the outlet gas was monitored by a zirconia oxygen sensor. In addition to the abovementioned condition, impedance spectra were corrected under $Ar+3\%H_2O$ atmosphere to examine the influence of the protonic conductivity. However, the bulk resistance values were found to be independent of moisture,

Table 1
Basic crystallographic data of (a) sample B [nominal composition: $Nd_{9.20}(SiO_4)_6O_{1.8}$] and (b) sample C [nominal composition: $(La_{0.46}Nd_{0.54})_{9.33}(SiO_4)_6O_2$], using high-resolution synchrotron X-ray diffraction measurements.

Site (Wyckoff)	Occp.	x	y	z	B_{eq}/B_{iso} (x 10^{-2} nm^2)
(a) sample B: $Nd_{9.33}(SiO_4)_6O_2$ [Nominal composition: $Nd_{9.20}(SiO_4)_6O_{1.80}$] $P6_3/m$, $a=0.956999(5)$ nm, $c=0.701895(3)$ nm $R_{wp}=3.398\%$, $R_p=2.440\%$, $R_R=5.989\%$, $R_{exp}=0.302\%$, $R_I=1.780\%$, and $R_F=0.787\%$.					
Nd1 (4f)	0.833	1/3	2/3	0.00018(10)	1.029
Nd2 (6 h)	1.0	0.24223(3)	0.01150(4)	1/4	0.510
Si (6 h)	1.0	0.37131(14)	0.40026(14)	1/4	0.590
O1 (6 h)	1.0	0.4841(3)	0.3220(3)	1/4	1.00(6)
O2 (6 h)	1.0	0.4725(3)	0.5950(3)	1/4	0.61(5)
O3 (12i)	1.0	0.2525(2)	0.3411(2)	0.0690(2)	1.51(4)
O4 (2a)	1.0	0	0	/1/4	1.42
(b) sample C: $(La_{0.440}Nd_{0.560})_{9.33}(SiO_4)_6O_2$ [Nominal composition: $(La_{0.46}Nd_{0.54})_{9.33}(SiO_4)_6O_2$] $P6_3/m$, $a=0.964079(4)$ nm, $c=0.708043(2)$ nm $R_{wp}=3.280\%$, $R_p=2.299\%$, $R_R=6.727\%$, $R_{exp}=0.325\%$, $R_I=2.086\%$, and $R_F=1.082\%$.					
Nd1 (4f)	0.833[a]	1/3	2/3	0.00054(10)	1.161
Nd2 (6 h)	1.0	0.24175(3)	0.01171(4)	1/4	0.687
Si (6 h)	1.0	0.37264(14)	0.40181(14)	1/4	0.92
O1 (6 h)	1.0	0.4875(3)	0.3217(4)	1/4	1.80(7)
O2 (6 h)	1.0	0.4728(3)	0.5970(3)	1/4	0.93(5)
O3 (12i)	1.0	0.2542(2)	0.3431(2)	0.0685(3)	2.09(5)
O4 (2a)	1.0	0	0	1/4	3.50

[a] Nd1: 0.366 La + 0.467(11); Nd2 : 0.44 La + 0.56 Nd.