

Oxide ion conduction mechanism in $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (RE=La, Nd) from neutron powder diffraction

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Abstract

The oxide ion conduction mechanism was clarified for high purity $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (RE=La and Nd) by Rietveld and maximum entropy method (MEM) analysis using neutron powder diffraction data collected at room temperature. All the compounds had an apatite-type structure in the space group $\text{P6}_3/\text{m}$. Neither site splitting nor interstitial sites of the oxide ion was observed. $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ had cation vacancies only at the $4f$ site. In $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$, the $4f$ sites were fully occupied by strontium and rare earths with a molar ratio of 1 : 1. Also, in $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$, the oxide ion at the hexagonal channel site had a large displacement along the c -axis. This large displacement is induced by cooperative rotation of SiO_4 tetrahedra around rare earths at the $4f$ site through oxide ion polyhedra around another rare earth at the $6h$ site. The displacement, enhanced by a vacancy in the $4f$ site, is directly related to oxide ion conduction in $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$.

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1. Introduction

Oxide ion conductors are very important for applications in solid oxide fuel cells and oxygen separators. Conventionally used oxide ion conductors have been stabilized zirconia with a fluorite structure [1] and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}$ perovskites [2]. Nakayama et al. reported high oxide ion conductivity in rare earth silicates $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ with an apatite structure [3,4]. The most attractive feature is that the conductivity of the oxide ions in the RE silicates at a relatively low temperature (below 600 °C) is much higher than that of stabilized zirconia. It has also been reported that conduction in the RE silicates is wholly ionic, with constant electrical conductivity across a wide range of oxygen partial pressures [5]. Single crystals of $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ with RE=Pr, Nd and Sm have been grown by the floating zone method [6–10]. Their oxide ion conductivities were anisotropic, i.e. the conductivity parallel to the c -axis in the hexagonal lattice was about one order of magnitude larger than that perpendicular to the c -axis. This anisotropy in conduction was related to

the crystal structure having an open channel along the c -axis (Fig. 1).

Another important feature is that $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ does not have an oxide ion vacancy which is essential for conventional oxide ion conductors. The apatite structure in $\text{P6}_3/\text{m}$ has 10 available sites for cations among both $4f$ and $6h$ sites in a unit cell. The RE silicates have 6.7% vacancy in their rare earth cation. The cation vacancy is necessary to maintain charge neutrality of the compound. In a recent computer modeling study, two kinds of oxide ion migration paths were proposed for $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$; a direct linear path through the hexagonal channel split sites and a non-linear sinusoidal-like migration through a new interstitial oxide ion site [12,13]. The importance of SiO_4 units for the conduction process was first raised by this modeling study, wherein, it was suggested that the conduction process was aided by cooperative displacements of the silicate substructure. Experimental doping studies have been performed to support this modeling in polycrystalline samples [14].

The purity of the sample is very important for the structure analysis because $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ is easily contaminated either with RE_2SiO_5 or $\text{RE}_2\text{Si}_2\text{O}_7$. Masubuchi et al. applied both neutron powder diffraction and single crystal X-ray diffraction for studying the structure refinements in high purity

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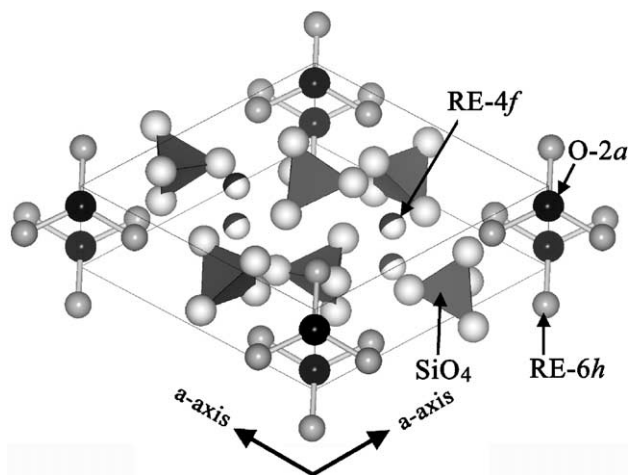


Fig. 1. Crystal structure of apatite-type rare earth silicate [11]. The oxide ions in the channel structure are coordinated with rare earth cations at RE-6h sites.

$\text{Nd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ crystal [11,15,16]. A significantly large anisotropic displacement parameter parallel to the c -axis was observed on the oxide ion in the $2a$ site in the channel. The site splitting and interstitial site of oxide ion proposed by other investigators were not detected by Masubuchi et al. Single crystal X-ray diffraction of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ confirmed the above results on structural analysis for the Nd-system in the apatite structure (space group $\text{P6}_3/\text{m}$) with no symmetry-lowering [17]. However, the high oxide ion conduction mechanism generated by the cation vacancy in $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ has not yet been fully understood.

It is well known that the maximum entropy method (MEM) can be used to create electron or nuclear density distribution maps from a set of structural factors without the use of any structure model. There have in fact been a number of studies on electron and nuclear density distributions using a combination of Rietveld refinement and MEM. For example, the ionic conduction path has been analyzed and visualized successfully for Li^+ in $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, O^{2-} in $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05})\text{O}_{2.8}$ [18,19].

In the present study, the oxide ion conduction mechanism was studied by visualizing the nuclear density distribution map by Rietveld and MEM analysis for high purity $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (RE=La and Nd) using neutron powder diffraction data collected at room temperature.

2. Experimental

High purity La_2O_3 , Nd_2O_3 , SrCO_3 and SiO_2 were used as starting materials. They were mixed in ethanol with an agate mortar. The mixture was calcined at 1200°C for 10 h and then sintered at 1650°C for 20 h. The ground product was rubber-pressed under 100 MPa pressure to discs and sintering again at 1650°C for another 20 h. The phase purity of the samples was confirmed by powder X-ray diffraction (PHILIPS, X'pert-MPD). The sintered discs were about 9 mm in diameter and 1.5 mm in thickness. Both disc sides were coated with Pt paste as electrodes. Electrical conductivity was measured using an AC impedance analyzer as described elsewhere [4].

High purity samples are required for reliable structure refinement. Therefore, $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ crystals were obtained by the floating zone method because they can congruently melt [20]. Neutron diffraction data was collected for powdered single crystals of $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The data of $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ was collected on their polycrystalline samples because they melted incongruently [11].

These measurements were performed at room temperature with a wavelength of 0.182035 nm in the Kinken powder diffractometer HERMES installed in the JRR-3M reactor at the Japan Atomic Energy Research Institute (JAERI), Tokai. The computer program RIETAN-2000 [21] was used for structural refinements. Nuclear density distributions were analyzed using the MEM program PRIMA [22]. The refined crystal structure and nuclear density images were visualized with the program VENUS [22] in three dimensions.

Structure refinements were carried out on the neutron powder diffraction data at room temperature similar to our previous reports [11]. A space group of $\text{P6}_3/\text{m}$ was applied without site splitting of the conducting oxide ion. For the refinement of $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (RE=La, Nd), a distribution of Sr and RE (molar ratio of 2:8) was employed for the two RE sites (4f and 6h) at the beginning. After convergence of their fractional coordinates, site occupancies of Sr and RE at the 4f and the 6h sites were refined.

3. Results and discussion

Electrical conductivity was measured for $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (RE=La and Nd) sintered compacts as a function of temperature. $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ showed the highest electrical conductivity among the materials tested, as shown in Fig. 2. The electrical conductivity of $\text{Sr}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ without cation vacancies was lower by about three orders of magnitude

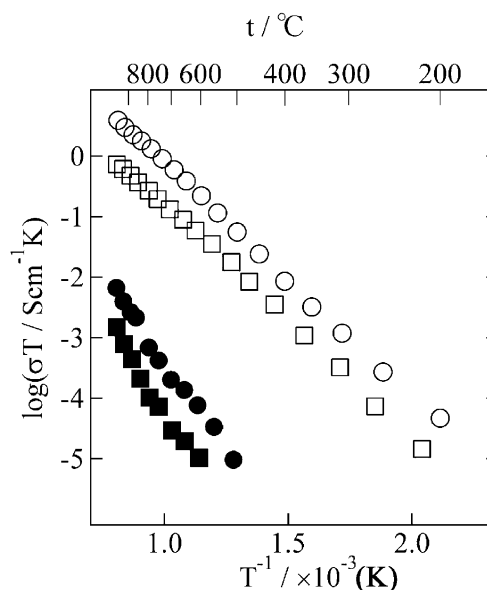


Fig. 2. Temperature dependence of electrical conductivity for sintered samples: (○) $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$; (●) $\text{Sr}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$; (□) $\text{Nd}_{9.33}(\text{SiO}_4)_6\text{O}_2$; (■) $\text{Sr}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$.

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