

Ionic Conductivity of $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ (Ln = La, Nd, Sm, Gd and Dy)

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Electrical properties were investigated for lanthanoid-silicates of $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ (Ln = La, Nd, Sm, Gd and Nd). The conductivity at 773 K was $2.3 \times 10^{-4} \text{ S cm}^{-1}$ for $\text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3$. The sole carrier is the O^{2-} ion, which was determined using an O_2 gas concentration cell.

Oxygen conducting electrolytes have widely been investigated for applications in fuel cells and oxygen gas sensors.^{1,2} One of the most important electrolytes is stabilized zirconia, which is well-known as an oxygen conducting electrolyte. We have reported that lanthanoid-silicates with alkali ions as an additive act as good alkali ionic conductors.³ The lanthanoid-silicate has a suitable tunnel size in its three-dimensional network structure for migration of the large K^+ ions.⁴ It is expected that large oxygen ions also easily migrate in the lanthanoid-silicate. We present the electrical properties of lanthanoid-silicates to develop new oxygen ionic conductors.

Ln_2O_3 (Ln = La, Nd, Sm, Gd and Dy) (99.9 % or 99.99 %) and SiO_2 (99.999 %) as starting materials were mixed using a ball-mill and calcined at 1773 K for 2 h in air. The obtained powders were ball-milled again with ethanol into fine powders,

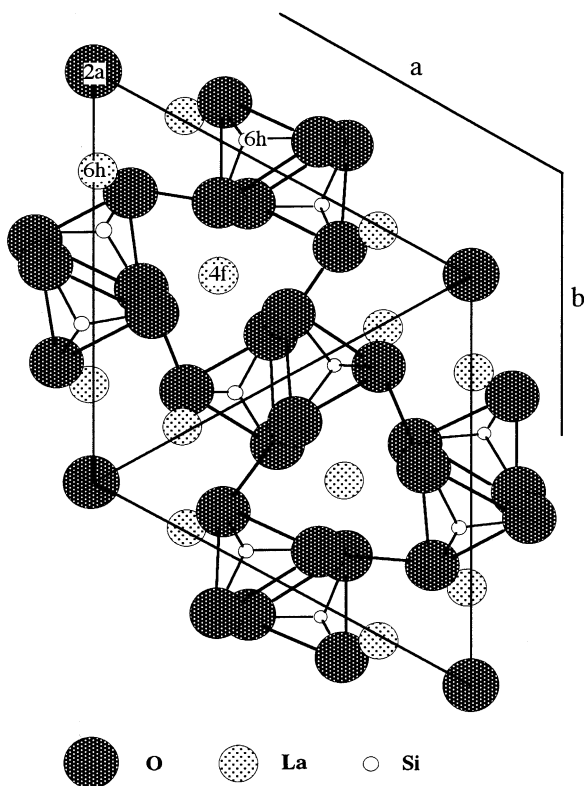


Figure 1. View of hexagonal structure of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$.

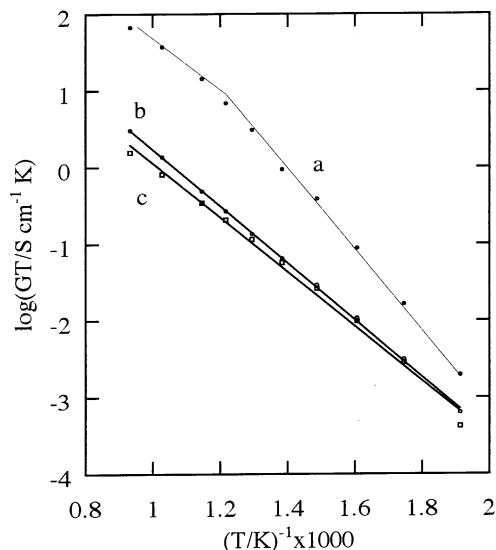


Figure 2. Temperature dependence of the conductivities determined by ac method.

a) stabilized zirconia, b) $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$, c) $\text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3$

to which some amount of 15 % of polyvinylalcohol solution was added. After drying, discs were pressed at 1000 kg cm^{-2} and sintered at 1823 K for 2 h in air. The relative density was 74 and 92 % for $\text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3$ and $\text{Sm}_{10}(\text{SiO}_4)_6\text{O}_3$, respectively. Platinum paint as electrodes was applied to opposite faces of the disc and heated at 1223 K. The equivalent total conductivities were measured in nitrogen for the samples pre-heated at 600 K in nitrogen to remove adsorbed water using a multi-frequency impedance meter in the frequency range of 100 ~ 10 MHz (Hewlett-Packard, 4292A).

A hexagonal phase was confirmed for $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ (Ln = La, Nd, Sm, Gd and Dy) samples. The crystal structure for the materials would be similar to that of $\text{La}_{4.67}(\text{SiO}_4)_3\text{O}$ (hexagonal, $a = b = 0.955 \text{ nm}$, $c = 0.74 \text{ nm}$)⁵ and of $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$ (JCPDS No.38-0283), because x-ray diffraction patterns for all the samples were in agreement with each other. This hexagonal structure is a three dimensional network structure connected by LnO_6 octahedra and SiO_4 tetrahedra. The hexagonal structure of the $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ sample derived from Rietvelt analysis is shown in Figure 1. The 2a position/site of oxygen is surrounded with six La ions. It is expected that the oxygen ions can migrate/jump to the neighboring other 2a positions.

Figure 2 shows temperature the dependence of the conductivity for $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ (Ln = La and Nd). A corresponding result for 8% Yb_2O_3 -stabilized zirconia (from Shinagawa Refractories Co. Ltd.) is also shown in the same Figure. The conductivity at 773

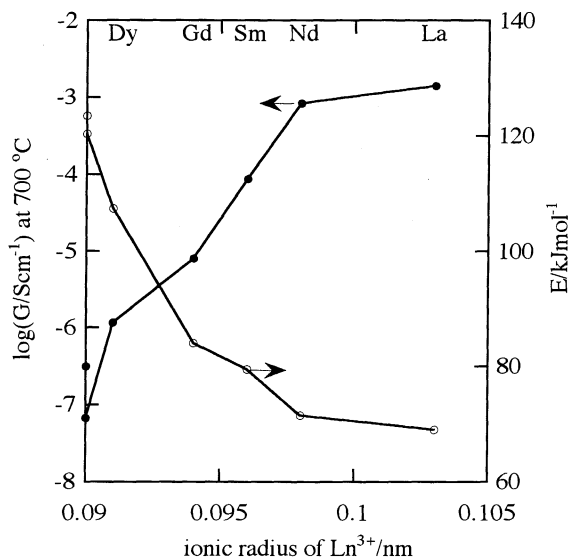


Figure 3. Relationship between ionic radius of Ln^{3+} and the electrical properties of $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ ($\text{Ln}=\text{La}, \text{Nd}, \text{Sm}, \text{Gd}$ and Dy).

K and the activation energy for ion migration are $2.3 \times 10^{-4} \text{ S cm}^{-1}$ and ca. 60 kJ mol^{-1} for $\text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3$, respectively. The conductivity of the Nd -sample is less than that of stabilized zirconia by a factor of about 10. In Figure 3, the relationship between ionic radius of Ln^{3+} and the electrical properties of $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}$ and Dy) with hexagonal phase are shown. The activation energy was increased and the conductivity was decreased by use of Ln with smaller ionic radii, in which the lattice constants of the a - and c -axes in the hexagonal phase decreased with decreasing Ln^{3+} ionic radius. The electrostatic contribution to the activation energy of conduction is represented by a relationship of the form:

$$E_B = Ae^2[(r_a + r_c)^{-1} - R^{-1}]$$

where A is a function of the dielectric constant, r_a and r_c are the radii of anion and cation, respectively, and R the distance between the ions when the mobile ion is halfway between adjacent equilibrium sites⁶. It is expected that the oxygen ion at the 2a position (see Fig.1) interacting with six Ln ions is mobile, and that the electrostatic energy of interaction between the oxygen in the 2a site and the six Ln^{3+} ions decreases with an increasing Ln^{3+} ionic radius. Qualitatively, the relationship between the ionic

Table 1. Theoretical and experimental values of RT/nF ($n=4$), electron transfer number (n) and ionic transport number (t_i) for O_2 gas concentration cell using $\text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3$ solid electrolyte

T (K)	RT/nF (theoretical) (mV)	RT/nF (observed) (mV)	n	t_i
873	18.37	18.4	4.0	1.0 ₀
973	20.50	21.9	3.8	1.0 ₇
1073	22.62	21.2	4.2	0.9 ₄

radius of Ln^{3+} and the activation energy is realized by the difference of the electrostatic interaction between the oxygen in the 2a position and the six Ln^{3+} ions in 6h positions.

An O_2 gas concentration cell, $\text{O}_2 + \text{Ar}, \text{Pt} / \text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3 / \text{Pt}, \text{Air} (21\% \text{O}_2)$ was used to confirm O^{2-} migration in the solid electrolyte. The EMF (electromotive force) between the two electrodes obeys the Nernst equation

$$\text{EMF} = (RT/nF) \ln (\text{Po}_2 / \text{Po}_2')$$

where R , T , n , F , Po_2 and Po_2' are the gas constant, the absolute temperature, the electron transport number, the Faraday constant, the O_2 partial pressure at the measuring electrode, and the O_2 partial pressure at the reference electrode ($\text{Po}_2' = 0.21$), respectively. The response time (90%) for the cell-EMF is ca. 1 min after change in the O_2 gas concentration at the measuring electrode. Table 1 summarizes theoretical and experimental Nernstian slopes (RT/nF), electron transfer number (n) and ionic transport number (t_i) for the O_2 gas concentration cell at various temperatures. The n value was almost in agreement with 4 for $\text{Nd}_{10}(\text{SiO}_4)_6\text{O}_3$ and $\text{Sm}_{10}(\text{SiO}_4)_6\text{O}_3$. The response is caused by the four-electron reaction of O_2 molecules at the electrodes. The results prove that the sole carrier in $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ is the O^{2-} ion.

References and Notes

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