Electrical Conductivity of Polycrystalline Li₂SiO₃ and γ -LiAlO₂

SATOSHI KONISHI and HIDEO OHNO

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11, Japan

Conductivities of polycrystalline Li₂SiO₃ and γ -LiAlO₂ were measured by the two-terminal ac method at $T = 450^{\circ}$ to 1000°C. Intrinsic and extrinsic regions were observed. The activation energies of conductivities in the extrinsic region for both samples agreed well with those of lithium diffusion obtained by T_1 analysis of nuclear magnetic relaxation.

I. Introduction

Some lithium compounds which exhibit lithium ion conduction have been studied as electrolyte materials. Recently, conductivity of Li₂O and its compounds,¹ lithium silicates and aluminosilicates,² lithium aluminate,³ and lithium-containing glass⁴ at temperatures lower than \approx 500°C were reported.

In this paper, the conductivity of polycrystalline metalithium silicate (Li₂SiO₃) and γ -lithium aluminate (LiAlO₂) was measured at temperatures up to 1000°C and the results were compared with those of NMR studies. The microscopic behavior of the lithium ion in these two materials, studied at temperatures up to 700°C using nuclear magnetic resonance (NMR), was reported previously.⁵ The activation energies of lithium diffusion were determined by analysis of the relaxation time T_1 of ⁷Li. They were 74.3 and 78.2 kJ/mol, respectively, for Li₂SiO₃ and γ -LiAlO₂. We also reported the conductivity of a single crystal and a sintered pellet of Li₂O⁶ and pointed out that the activation energy of conductivity in the extrinsic region agreed with that determined by NMR.

II. Experimental Procedure

(1) Sample Preparation

The Li₂SiO₃ and LiAlO₂ powders were obtained as follows. The appropriate oxides were mixed and heated to 1200°C in air for a few hours and the phases were determined by X-ray diffraction (XRD) using CuK α Ni-filtered radiation. All the diffraction patterns in Li₂SiO₃ fit an orthorhombic structure and those in LiAlO₂ fit a tetragonal structure γ -LiAlO₂. The analytical data of these two samples are listed in Table I.

Fused polycrystalline pellets were used to measure conductivities of Li₂SiO₃ or γ -LiAlO₂. Li₂SiO₃ or LiAlO₂ powder was melted at 1400° or 1650°C in a platinum crucible in dry air with an electric furnace, then quenched to room temperature. All the XRD patterns of the fused pellet of LiAlO₂ fit tetragonal γ -LiAlO₂.

The pellets were 2 mm wide by 7 mm long by 1.5 mm thick for Li_2SiO_3 and 4 mm wide by 4.5 mm long by 2.9 mm thick for γ -LiAlO₂.

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Table I. Spectrographic Analyses of Powders Studied

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Impurities in LiAlO ₂ (wt%)		Impurities in Li ₂ SiO ₃		
Na 0.065 K <0.001 Mg<0.001 Ca <0.002	Cu<0.001 Fe<0.001 Ni<0.001 Cr<0.001	Na 0.008 K <0.001 Ag <0.001 Ca 0.013	A1 0.003 Fe 0.003 Cr <0.001 Cu 0.001	
Ag <0.001 Si <0.001	Pb<0.001	Mg<0.001 Pb <0.001	Ni 0.001	

(2) Measurements

Sample conductivities were measured by the two-terminal ac method. The platinum electrodes were made from paste attached to both surfaces and baked at $\approx 500^{\circ}$ C. The thickness was a few micrometers. Electrical contact was made by clamping the sample between platinum foil disks in a boron nitride (BN) cell, which was loaded in a quartz tube and heated by an electric furnace in dry argon.

The ac measurements were made using one or more of three bridges: a Wheatstone bridge at 1 kHz, an LCR meter with a frequency range of 0.1 to 100 kHz, and a direct reading impedance bridge and lock-in amplifier using a frequency sign wave of 1 to 200 kHz obtained using a function generator.

III. Results and Discussion

Figure 1 shows some typical data of the complex impedance plot of Li_2SiO_3 for a frequency of 0.1 to 100 kHz at 484°, 526°, 561°, 895°, and 952°C. The bulk resistance is identified from the intersecting point of a semicircle with the real axis. The difference between the real component of impedance at 1 kHz and the bulk resistance was small in this sample.

Figure 2 shows some typical data of complex impedance plots of γ -LiAlO₂ at 442°, 454°, 538°, 563°, and 608°C. There were differences between the real component of impedance at 1 kHz and bulk resistance at low temperatures. Based on this result, complex impedance plots were made in each measurement in order to identify bulk resistances in γ -LiAlO₂.

For polycrystalline LiAlO₂, the fused pellet was crushed to powder after conductivities were measured and XRD analyses were made. All of the diffraction patterns fit the tetragonal structure of γ -LiAlO₂. The results showed that the tetragonal structure was retained during measurements of electrical conductivity.

Figure 3 shows the relation between temperature and conductivity multiplied by temperature (σT) for Li₂SiO₃ and γ -LiAlO₂,



Fig. 1. Complex impedance plot for Li₂SiO₃.



Fig. 2. Complex impedance plot for γ -LiAlO₂.

compared with single-crystal Li₂O. Two relations are seen in the lower and higher temperatures for each sample. Since there were no phase transitions in these materials in this temperature range, they are identified as intrinsic and extrinsic regions.

For Li_2SiO_3 , activation energies E, obtained with relation $\sigma T = A \exp(-E/RT)$ in extrinsic and intrinsic regions, were 73.3 and 185.3 kJ/mol, respectively. The transition temperature from the extrinsic to the intrinsic region T_{tr} was 826°C. Raistrick et al.² reported that the activation energy for Li₂SiO₃ is 92.6 kJ/mol at $T = 200^{\circ}$ to 600°C. The present data had higher conductivities and lower activation energies than those of Raistrick et al., possibly because they used a sintered pellet to measure electrical conductivity.

For γ -LiAlO₂, activation energies in the extrinsic and intrinsic regions were 78.2 and 121.6 kJ/mol, respectively, and T_{tr} was 763°C. The electrical conductivities of these three materials are summarized in Table II.

Diffusion of the lithium ion, which causes ionic conduction in these materials, has also been observed with pulsed nuclear magnetic resonance at temperatures up to 700°C.⁵ The motional narrowing of the absorption peak was observed at 400° to 450°C and 500° to 550°C, respectively, for Li₂SiO₃ and γ -LiAlO₂, where the inverse of relaxation time T_1^{-1} began to increase. The activation energies for T_1^{-1} were found to be 74.3 and 78.2 kJ/mol, respectively, for Li₂SiO₃ and γ -LiAlO₂.⁵ These values agree well with those of activation energies of conductivities in the extrinsic region, observed in the present study.

IV. Summary

The conductivities of polycrystalline γ -LiAlO₂ and Li₂SiO₃ were measured at $T = 450^{\circ}$ to 1000°C. The activation energies in the extrinsic and intrinsic regions of conductivities were, respectively, 78.2 and 121.6 kJ/mol, and the transition temperature was 763°C for polycrystalline γ -LiAlO₂. Those for Li₂SiO₃ were 73.3 and 185.3 kJ/mol and 826°C. The activation energies for the extrinsic regions agreed with those obtained by NMR studies. Thus, it is concluded that electrical conductivity in these materials is caused by lithium diffusion.



Fig. 3. Conductivity, σT , of polycrystalline Li₂SiO₃ and y-LiAlO₂ compared with that of single-crystal Li₂O as a function of reciprocal temperature. Monofrequency data $(\bigcirc = 1 \text{ kHz})$ and frequency-independent conductivity data $(\Delta = \text{corrected for frequency dependence}).$

Table II. Electrical Conductivities of Polycrystalline Li₂SiO₃ and y-LiAlO₂ and Single-Crystal Li₂O*

	Extrinsic		Transition	Intrinsic	
	A	E	temp. (°C)	A	Ε
Li ₂ O (single-c	9.25×10^2	50.2	636	5.45×10^{6}	116.8
Li_2SiO_3 γ -LiAlO ₂	6.07×10^2 3.62×10^2	73.3 78.2	826 763	3.17×10^{8} 5.54×10^{4}	185.3 121.6

 $*\sigma \overline{T} = A \exp(-E/RT); \sigma \text{ in } \Omega^{-1} \cdot \text{cm}^{-1}, T \text{ in } K, A \text{ in } \Omega^{-1} \cdot \text{cm}^{-1} \cdot K, E \text{ in } kJ/mol.$

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