JOURNAL OF SOLID STATE CHEMISTRY **58**, 401–403 (1985)

Ionic Conductivity of $Li_2MgSn_3O_8$ Ramsdellite

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Received October 26, 1984

The ionic conductivity of polycrystalline pellets of $Li_2MgSn_3O_8$ with ramsdellite-type structure was measured by complex impedance technique. The conductivity is 1.2×10^{-8} $(\Omega\ cm)^{-1}$ at 300°C and 2.3×10^{-4} $(\Omega\ cm)^{-1}$ at 450°C. The results are discussed in relation to structural properties.

Introduction

$Li_2MgSn_3O_8$ appears to be isostructural with γ-MnO_2 ramsdellite (*1*). The projection of the ramsdellite structure along [100] is shown in Fig. 1 (Ref. (*2*)). $Li_2Ti_3O_7$ and $LiFeSnO_4$ also have crystal structures that are derived from ramsdellite (*3–5*). The ramsdellite lattice is built up of edge-sharing metal–oxygen octahedra that form infinite double chains. The double chains share corners with adjacent chains to form a three-dimensional framework. Between adjacent chains are empty tunnels which can be occupied by Li^+ ions. In $Li_{1.5}[Li_{0.5}Ti_3]O_7$, $0.5Li^+$ and $3Ti^{4+}$ ions are randomly distributed over the octahedral sites of the framework structure and $1.5Li^+$ ions occupy sites in the tunnels (*3*). In $LiFeSnO_4$ a random distribution of Fe^{2+} and Sn^{4+} ions form the framework, and all the Li^+ ions are located in the tunnels (*4, 5*). A maximum of four *A* cations may be located in the tunnels, based on distances between two possible neighhboring sites, leading to the limiting formula $A_4B_4O_8$ (*4*). Thus in $Li_2Ti_3O_7$, $LiFeSnO_4$ and possibly in $Li_2MgSn_3O_8$ the tunnels of the ramsdellite are partially occupied. Therefore high mobility of Li^+ ions is expected in these compounds.

The ionic conductivity of polycrystallin $Li_2Ti_3O_7$ is $\sim 10^{-2}$ $(\Omega\ cm)^{-1}$ at 450°C (*6*), and reversible lithium insertion has been demonstrated in $LiFeSnO_4$ (*7*). In this communication we report the results of ionic conductivity measurements of $Li_2MgSn_3O_8$.

Experimental

The $Li_2MgSn_3O_8$ was prepared from a stoichiometric mixture of $Mg(NO_3)_2 \cdot 6H_2O$, SnO_2 and excess Li_2CO_3, to prevent loss of Li_2O, in an alumina crucible inside a electric crucible furnace. The temperature of the furnace was raised slowly from 100 to 600°C in order to expel the gases, and left at

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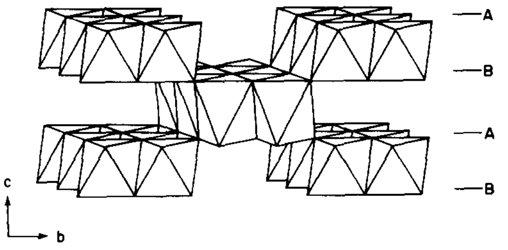

FIG. 1. Projection of the ramsdellite structure along [100].

600°C for a few hours, and then increased to 900°C for several hours. The sample was then air-quenched to room temperature, reground, and heated again at 1100°C for several hours, after which it was again air-quenched to ambient temperature. Any excess Li_2O present in the final product was leached out with water.

The X-ray powder diffraction patterns of the products were examined using nickel-filtered copper radiation.

Pellet samples for ionic conductivity measurements were prepared by weighing out 0.50 g powder and compressing to 3.17 mm in height and 6.18 mm in diameter at 15,000 lbs/in.^{2}. The cylindrical pellets were sintered at 1150°C for 2½ hr in air then quenched to room temperature. The pellets were covered with the sample powder to prevent loss of Li_2O during the sintering process. The X-ray diffraction pattern of the sintered samples was checked to confirm the identity of phases present. Weight loss was not observed after the sintering process. Both surfaces of the pellets were polished with silicon carbide paper (No. 400) and sputtered with ~2000 Å Au. The ionic conductivity was measured by complex impedance technique as reported previously (*8*). Elemental analysis for Li, Mg, and Sn was obtained by a Beckman plasma emission spectrometer.

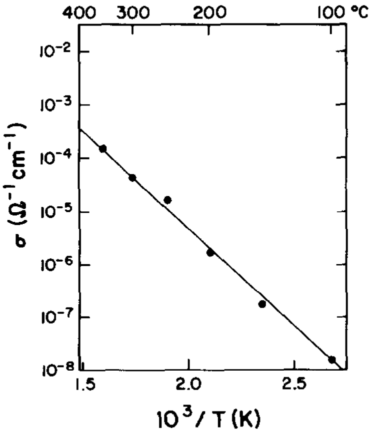

FIG. 2. Temperature variation of the conductivity (σ) of polycrystalline pellets of $Li_2MgSn_3O_8$.

Results and Discussion

The X-ray powder diffraction pattern of our product agreed well with that of Keller and West (*1*) reported for a phase of approximate composition, $Li_2MgSn_3O_8$. Results of the elemental analysis of our samples confirmed this stoichiometry.

Figure 2 shows the temperature variation of the conductivity. The highest ionic conductivity of $2.3 \times 10^{-4}\ (\Omega\ cm)^{-1}$ is observed at 450°C. Above this temperature the compound decomposes and the conductivity decreases. A least-squares fit of the data to the equation $\sigma = \sigma_0 \exp(-E_a/RT)$ yielded the activation energy, $E_a = 0.76$ eV in the temperature region 100–400°C.

The ionic conductivity of polycrystalline samples of $Li_2Ti_3O_7$ is two orders of magnitude larger at the same temperature ($\sim 10^{-2}\ (\Omega\ cm)^{-1}$). The atomic distribution corresponding to $[Li_{1.72}\square_{2.28}]\ [(Ti_{3.43}Li_{0.57})O_8]$ where $\square$ are vacancies, or $[Li_{2.29}\square_{1.71}]\ [(Ti_{3.43}\square_{0.57})O_8]$ fit the diffraction data almost equally well (*6*). The anisotropy of ionic conductivity observed in single crystals supports the latter formula (*6*). In the $Li_2MgSn_3O_8$ ramsdellite the atomic distribution $[Li_2\square_2]\ [(MgSn_3)O_8]$ is expected. It is possible that the large difference observed in the ionic conductivity of these two compounds is due to the fact that $Li_2MgSn_3O_8$ is a one-dimensional conductor, while in $Li_2Ti_3O_7$ the conductivity is three-dimensional.

Acknowledgment

This work was supported in part by the Office of Naval Research.

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