

BRIEF COMMUNICATION

Ionic Conductivity of Li_7BiO_6

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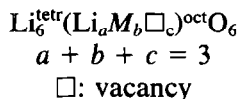
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The ionic conductivity of polycrystalline Li_7BiO_6 pellets has been measured by complex impedance method. The conductivity is $5.7 \times 10^{-3} (\Omega \text{ cm})^{-1}$ at 300°C and $3.8 \times 10^{-6} (\Omega \text{ cm})^{-1}$ at 100°C . Li_7BiO_6 is the best lithium conductor among the structurally related Li_nMO_6 compounds.

Introduction

Recently the ionic conductivities of Li_8ZrO_6 , Li_8SnO_6 , Li_8HfO_6 , Li_8CeO_6 , Li_7NbO_6 , Li_7TaO_6 , and $\text{Li}_6\text{In}_2\text{O}_6$ have been measured and the highest Li^+ conductivities were observed in the Li_7MO_6 phases (1-3). The lithium hexaoxometallates may be formulated as Li_nMO_6 with $n = 6, 7$ or 8 , and $M =$ a large variety of metal ions from group III through group VIII. The structure of Li_nMO_6 is characterized by octahedral sheets of CdI_2 type, between which 6Li^+ ions are inserted in a tetrahedral environment as



The structure is pseudo two-dimensional and the lithium ion mobility is significantly larger in the octahedral layers as indicated by ^7Li NMR measurements (4); thus the

highest lithium conductivities are observed as expected in the Li_7MO_6 compounds ($\text{Li}_6[\text{LiM}\square]\text{O}_6$) vs $\text{Li}_6[\text{Li}_2\text{M}]\text{O}_6$ in Li_8MO_6 , (3)) and of these Li_7TaO_6 was shown to be the best conductor with $\sigma = 1.1 \times 10^{-4} (\Omega \text{ cm})^{-1}$ at 200°C (3).

Li_7BiO_6 is isostructural with the Li_nMO_6 phases (5); its hexagonal unit cell, $a = 5.50 \text{ \AA}$ and $c = 15.45 \text{ \AA}$, is considerably larger than that of Li_7TaO_6 ($a = 5.39 \text{ \AA}$, $c = 15.11 \text{ \AA}$), and it is thermally stable up to 600°C . Therefore, high ionic conductivity might be expected.

In this paper, we report the results of ionic conductivity measurements of Li_7BiO_6 .

Experimental

Starting materials were reagent grade Bi_2O_3 and Li_2O which was obtained by the thermal decomposition of anhydrous Li_2O_2 in vacuum at 450°C for 6 hr. Stoichiometric compositions were thoroughly mixed in an agate mortar in a He dry box according to the equation:



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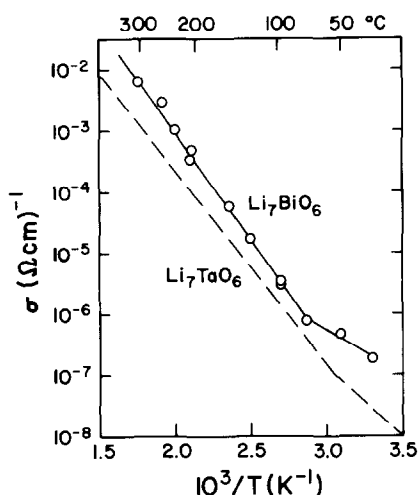


FIG. 1. Variation of conductivity with inverse temperature of Li_7BiO_6 and Li_7TaO_6 .

The mixtures were pressed into cylindrical pellets 9.5 mm diameter and about 5 mm thick at 15,000 lbs/in². The pressed pellets were transferred to high-purity alumina crucibles, were embedded in excess Li_2O powder in order to minimize the Li_2O losses, and were heated at 700°C for 18 hr in air. After cooling, the pellets were crushed and examined by X-ray powder diffraction using a Norelco diffractometer with Ni-filtered copper radiation. Lithium content was determined by atomic absorption spectrophotometric methods.

Pellet samples for ionic conductivity measurements were prepared by pressing to 6.35 mm diameter and about 4 mm thickness at 30,000 lbs/in² followed by sintering at 800°C for 18 hr in air and quenching in air. Again, Li_2O loss was minimized by covering the pellets with Li_2O powder during the sintering process. The X-ray diffraction pattern and lithium content of the sintered samples were checked to confirm the identity and composition of the phases present. Weight loss was not observed after sintering. The density of the sintered pellets was

about 80% of theoretical value. Both surfaces of the pellets were polished using silicon carbide (No. 400) paper and sputtered with about 1 μm of gold followed by a coating of silver paint (Engelhard No. 16).

The ionic conductivities were measured as reported previously (3).

Results and Discussion

Figure 1 shows the conductivity δ versus $1/T$ plot for Li_7BiO_6 and Li_7TaO_6 (3). The higher ionic conductivity is observed in Li_7BiO_6 : 5.7×10^{-3} ($\Omega \text{ cm}$)⁻¹ at 300°C and 3.8×10^{-6} ($\Omega \text{ cm}$)⁻¹ at 100°C. Different activation energies (E_a) corresponding to a lower and higher temperature region are observed, 0.21 and 0.68 eV, respectively. The change in the slope of the δ vs $1/T$ plot of Li_7BiO_6 is probably due to a transition from extrinsic to intrinsic mechanism of conductivity. E_a in the high temperature region is close to that of Li_7TaO_6 (0.67 eV (3) or 0.66 eV (1)). This is somewhat surprising, as with the increased size of the Bi(V) ion, 0.76 vs 0.64 Å for Ta(V) (Ref. (6)). The channel size for passage of the lithium ion is expected to be optimized in Li_7BiO_6 , and the energy barrier for ion jumps from occupied to vacant sites should be lowered significantly.

The fact that the activation energies of conductivity are similar (~ 0.67 eV) for all of the Li_7MO_6 compounds (Li_7TaO_6 , Li_7NbO_6 , Li_7BiO_6) measured so far, explains why we do not observe large improvements (i.e., an order of magnitude or larger) in the ionic conductivity from compound to compound.

Acknowledgments

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