Ionic Conductivity of Li$_7$Bi$_6$

By
E. Nomura and M. Greenblatt

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Rutgers, The State University of New Jersey
Department of Chemistry
New Brunswick, N.J. 08903

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The ionic conductivity of polycrystalline \( \text{Li}_7\text{BiO}_6 \) pellets has been measured by complex impedance method. The conductivity is \( 5.7 \times 10^{-2} \text{(S/cm)}^{-1} \) at 300°C and \( 3.8 \times 10^{-3} \text{(S/cm)}^{-1} \) at 100°C. \( \text{Li}_7\text{BiO}_6 \) is the best lithium conductor among the structurally related \( \text{Li}_2\text{MO}_6 \) compounds.
Ionic Conductivity of Li7BiO₆

E. Nomura* and M. Greenblatt
Department of Chemistry
Rutgers the State University of New Jersey
New Brunswick, N.J. 08903

ABSTRACT:
The ionic conductivity of polycrystalline Li7BiO₆ pellets has been measured by complex impedance method. The conductivity is 5.7x10⁻³(Ωcm)⁻¹ at 300°C and 3.8x10⁻⁶(Ωcm)⁻¹ at 100°C. Li7BiO₆ is the best lithium conductor among the structurally related Li₇MO₆ compounds.

Introduction

Recently the ionic conductivities of Li₆ZrO₆, Li₆SnO₆, Li₆HfO₆, Li₆CeO₆, Li₆NbO₆, Li₆TaO₆ and Li₆In₂O₆ have been measured and the highest Li⁺ conductivities were observed in the Li₇MO₆ phases.¹⁻³ The lithium hexa-z-tallates may be formulated as Li₇MO₆ with n = 6, 7 or 8, and M = a large variety of metal ions from group III through group VIII. The structure of Li₇MO₆ is characterized by octahedral sheets of CdI₂ type, between which 6Li¹⁺ ions are inserted in a tetrahedral environment as

Li⁺₆(\text{tetra})\{Li₆Mₕ \Box_c \text{oct})₆
a + b + c = 3
\Box: \text{vacancy}

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 Li₇MO₆ compounds (Li₆[Li₂Mₕ]₀₆) vs Li₆[Li₂Mₕ]₀₆ in Li₇MO₆ (3) and of these Li₇TaO₆ was shown to be the best conductor with σ = 1.1x10⁻⁴(Ωcm)⁻¹ at 200°C (3).

Li₇BiO₆ is isostuctural with the Li₇MO₆ phases (5); its hexagonal unit cell, a = 5.35Å and c = 15.43Å, is considerably larger than that of Li₇TaO₆ (a = 5.39Å, c = 15.11Å), 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\(_7\)Bi\(_2\)O\(_6\).

**Experimental**

Starting materials were reagent grade Bi\(_2\)O\(_3\) and Li\(_2\)O which was obtained by the thermal decomposition of anhydrous Li\(_2\)O\(_2\) in vacuum at 450°C for 6 hours. Stoichiometric compositions were thoroughly mixed in an agate mortar in a He dry box according to the equation:

\[
7\text{Li}_2\text{O} + \text{Bi}_2\text{O}_3 + \text{O}_2 \rightarrow 2\text{Li}_7\text{Bi}_2\text{O}_6
\]

The mixtures were pressed into cylindrical pellets 9.5 mm diameter and about 5 mm thick at 15,000 lbs/in\(^2\). The pressed pellets were transferred to high purity alumina crucibles, were embedded in excess Li\(_2\)O powder in order to minimize the Li\(_2\)O losses, and were heated at 700°C for 18 hours 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.

Pallet samples for ionic conductivity measurements were prepared by pressing to 6.35 mm diameter and about 4 mm thickness at 30,000 lbs/in\(^2\) followed by sintering at 800°C for 18 hours in air and quenching in air. Again, Li\(_2\)O loss was minimized by covering the pellets with Li\(_2\)O 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 were about 80% of theoretical value. Both surfaces of the pellets were polished using silicon carbide (#400) paper and sputtered with about 1 µm of gold followed by a coating of silver paint (Engelhard #16).

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

**Results and Discussion**

Figure 1 shows the conductivity \(\delta\) versus 1/T plot for Li\(_7\)Bi\(_2\)O\(_6\) and Li\(_7\)TaO\(_6\) (3). The higher ionic conductivity is observed in Li\(_7\)Bi\(_2\)O\(_6\): 5.7 x 10\(^{-3}\)(Qcm\(^{-1}\)) at 300°C and 3.8 x 10\(^{-3}\)(Qcm\(^{-1}\)) at 100°C. Different activation energies \(E_a\) corresponding to a lower and higher temperature region are observed, 0.21 eV and 0.68 eV respectively. The change in the slope of the \(\delta\) vs 1/T plot of Li\(_7\)Bi\(_2\)O\(_6\) 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\(_7\)TaO\(_6\) (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 Å 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\(_7\)Bi\(_2\)O\(_6\), 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\(_7\)MO\(_6\) compounds (Li\(_7\)TaO\(_6\), Li\(_7\)NbO\(_6\), Li\(_7\)BiO\(_6\)) 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.
Fig. 1
Variation of conductivity with inverse temperature
of Li7BiO6 and Li7TaO6

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*Present address: Central Laboratory, Yuasa Battery Co. Ltd. Takatsuki Osaka, Japan.


