

ELECTRICAL CONDUCTIVITY OF A NEW SOLID ELECTROLYTE GLASS MATERIAL $\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$

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(Received January 27, 1984; in revised form March 13, 1984)

Summary

With a view to the development of a lithium-borate based glass material with high ionic conductivity at the lowest possible temperature, the conductivities of different compositions of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glass system have been studied. The effect of LiNbO_3 addition on the temperature dependent conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ (40:60 mol%) system, which shows maximum conductivity within the homogeneous glass formation region, was observed. The enhancement in the conductivity, $1.43 \times 10^{-2} \text{ (ohm cm)}^{-1}$ at 623 K, has been attributed to the increase in Li ion concentration and to its mobility which is due to vacant sites provided by the pentavalent Nb ion of Nb_2O_5 . The conductivities achieved in the present investigation have been compared with earlier reports on similar systems. This material may be suitable as an electrolyte for application to power sources.

Introduction

The increased interest in fast ionic conductors (FICs) is, to a great extent, due to their possible application to power sources or other electrochemical devices. Until recently, crystalline, solid electrolytes were extensively studied. Most recently, however, a number of investigators have reported fast ionic conduction in lithium-borate glasses [1 - 15]. FIC in glasses provides the possibility of utilizing such glasses for batteries where their ease of fabrication into complex and thin-walled structures can result in significant advantages over their polycrystalline counterparts.

Considerable interest has recently been shown in materials in which ferroelectric crystals are precipitated in glass to produce pore-free dielectrics [16]. Lithium niobate is a known ferroelectric material. Ionic conductivity has been invoked to explain the high temperature conductivity data of the compound [17]. Marked enhancement of ionic conductivity has been observed in rapidly quenched LiNbO_3 glass without any network forming additives [13]. The addition of a network former was considered to be useful because these additions give particle size control and structural continuity [14].

In the present study $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ (40:60 mol%) gave the best homogeneous glass-forming composition, with considerably increased ionic conductivity, of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ series. Further, the addition of LiNbO_3 beyond 10 mol%, at the cost of B_2O_3 , raises the melting point of the system. Hence, the addition of 10 mol% of LiNbO_3 was incorporated: (i) to lower the temperature of glass formation; (ii) to avoid inhomogeneity; (iii) to improve the ionic conduction resulting from the increased cation concentration in the glass system.

Taking all the above facts into account, the present investigation was aimed at the production of a lithium-borate based glass material with a high ionic conductivity at the lowest possible temperature. With this in view, the electrical conductivity of the $\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$ (40:10:50 mol%) glass system was studied at 1 kHz in the temperature range 373 - 673 K. Bulk conductivity values at different temperatures have been extracted by means of conventional complex impedance analysis. The results have been compared with previous reports.

Experimental

B_2O_3 , A.R. (99% pure), as supplied by SISCO (India), and Li_2CO_3 (99.9% pure, Moscow, USSR) were used as starting materials. Four batches, consisting of 30:70, 40:60, 50:50, and 60:40 mol% $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, were prepared.

LiNbO_3 single crystals, grown by slow cooling of the melt and having a starting composition of Li_2CO_3 and Nb_2O_5 (99.9% pure, A. G. Fluka, Switzerland) in 1:1 molar ratio, as reported earlier [18], were used in the preparation of the $\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$ (40:10:50 mol%) glass system.

About 12 g of the raw materials of each batch were weighed (with an accuracy of 0.0001 g) and mixed thoroughly under acetone in an agate mortar. The dried mixture was heated in a porcelain crucible, at a moderate rate, in an electric furnace. The temperature was raised to 1223 K. The melt was held at this temperature for 2 h for homogenization. The glasses were cast by quenching the melt at room temperature into an aluminium mould. No contamination of the glasses by the aluminium mould was observed. Within the glass-forming range, these glasses were colourless and transparent. They were annealed at 573 K for 2 h. The formation of glass was confirmed by the X-ray diffraction technique. The glasses thus obtained were polished flat to obtain rectangular samples of dimensions $9 \times 6 \times 2$ mm. To achieve ohmic contact with the sample holder electrodes, the flat surfaces of the samples were silver painted and baked at 473 K for 2 h.

The a.c. electrical conductivity was measured with a Universal impedance bridge, TF 2700 AIMIL (India), at 1 kHz with an accuracy of $\pm 2\%$ in the temperature range 373 - 673 K. The conductivity measurements were recorded during the cooling cycle using the two terminal method. The sample was enclosed in a shielded holder, provided with silver electrodes, under

light spring tension with a thermocouple mounted close to it to monitor the temperature.

To ascertain the nature of the polarization, the vector impedance, Z , of the sample was measured at different temperatures and frequencies ranging from 373 to 673 K and from 20 Hz to 50 kHz, respectively, by means of a well-known three voltage method, using an oscillator, an a.c. millivoltmeter and a standard non-inductive resistance. The sample, audio frequency (A.F.) oscillator, and a standard non-inductive decade resistance box were connected in series. The voltages V_a , V_R and V_s across the output of the audio-oscillator, the appropriate resistance in a decade resistance box, and the sample, respectively, were measured by an a.c. millivoltmeter (Simpson). The appropriate resistance value was selected so that it was comparable with that of the sample. V_a , V_R and V_s were such that $V_R + V_s > V_a$ and could be represented by the three sides of a triangle using a suitable scale. Further, V_s was resolved into two perpendicular components $V_s \cos \theta$ and $V_s \sin \theta$ so that

$$V_s \cos \theta / I = Z \cos \theta = Z'$$

and

$$V_s \sin \theta / I = Z \sin \theta = Z''$$

where

$$I = V_R / R$$

Results and discussion

Figure 1 depicts the plots of $\log(\sigma T)$ vs. $10^3/T$ for different compositions of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system. The conductivity values for these compositions at 473 and 623 K, along with their characteristics, are reproduced in Table 1. In this series, the sample of composition 60:40 mol% shows the maximum conductivity, but since this composition did not give a homogeneous glass, it was discarded for further studies.

Of the remaining three compositions, 40:60 mol% gave the maximum conductivity. This composition has more Li ion charge carriers, as well as sufficient vacant sites provided by B_2O_3 , in comparison with the 30:70 mol% sample. By contrast, in the case of the 50:50 mol% composition, in spite of increased Li ion carriers, the reduction in B_2O_3 results in a smaller number of vacant sites which, in turn, reduces the mobility of the Li ion. Hence, the 40:60 mol% composition was selected for further investigation.

Figure 2 illustrates the effect of the addition of LiNbO_3 on the temperature dependent conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ (40:60 mol%) system. The typical conductivity values at 473 and 623 K are listed in Table 2, which illustrates the enhancement of conductivity by almost two orders of magnitude after incorporation of LiNbO_3 in the system. This is attributed to the

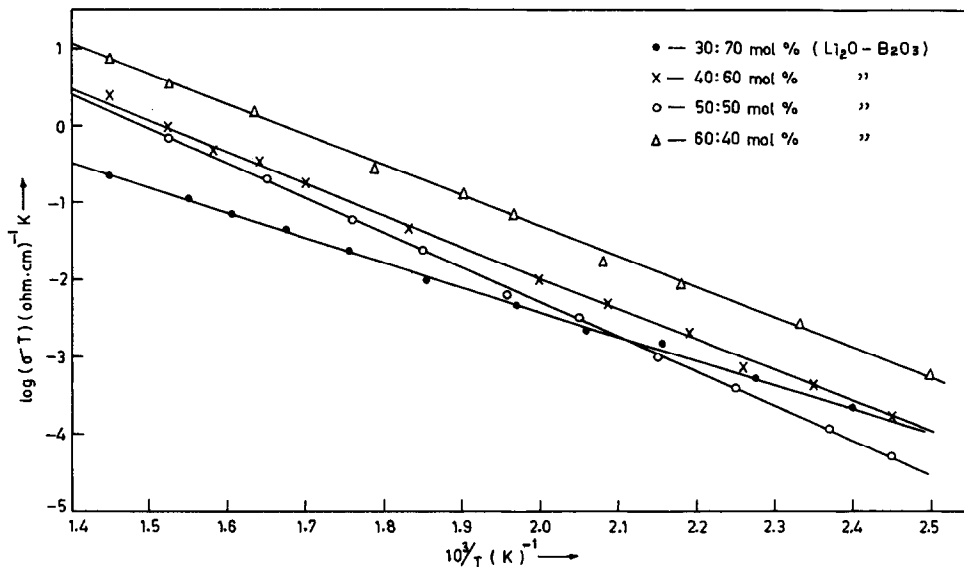


Fig. 1. Variation of the electrical conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system with temperature.

TABLE 1

Variation of conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system as a function of composition at 473 and 623 K with their apparent characteristics

System	Characteristics	Conductivity (ohm cm^{-1})
$\text{Li}_2\text{O}-\text{B}_2\text{O}_3$		
30:70 mol%	Homogeneous glass Hygroscopic	$\sigma_{(473 \text{ K})} = 3.39 \times 10^{-6}$ $\sigma_{(623 \text{ K})} = 1.15 \times 10^{-4}$
40:60 mol%	Homogeneous glass	$\sigma_{(473 \text{ K})} = 6.38 \times 10^{-6}$ $\sigma_{(623 \text{ K})} = 6.84 \times 10^{-4}$
50:50 mol%	Homogeneous glass	$\sigma_{(473 \text{ K})} = 6.01 \times 10^{-6}$ $\sigma_{(623 \text{ K})} = 5.76 \times 10^{-4}$
60:40 mol%	Tends towards crystalline nature	$\sigma_{(473 \text{ K})} = 1.13 \times 10^{-5}$ $\sigma_{(623 \text{ K})} = 2.66 \times 10^{-3}$

fact that LiNbO_3 provides: (i) additional Li ions, and (ii) excess available vacant sites due to the presence of pentavalent Nb ion. This is in agreement with other reports on a similar system [13].

Figure 3 shows the complex impedance plots for the sample containing LiNbO_3 at 443, 493, 569 and 600 K. The bulk impedance (usually modelled by a parallel $R-C$ network) is conventionally attributed to the low impedance semicircle, while the electrode impedance is attributed to the high impedance semicircle [15].

Both semicircles are readily observed in the 443 K isotherm (Fig. 3(a)). The bulk resistance is identified by the point on the real axis at which the two semicircles meet.

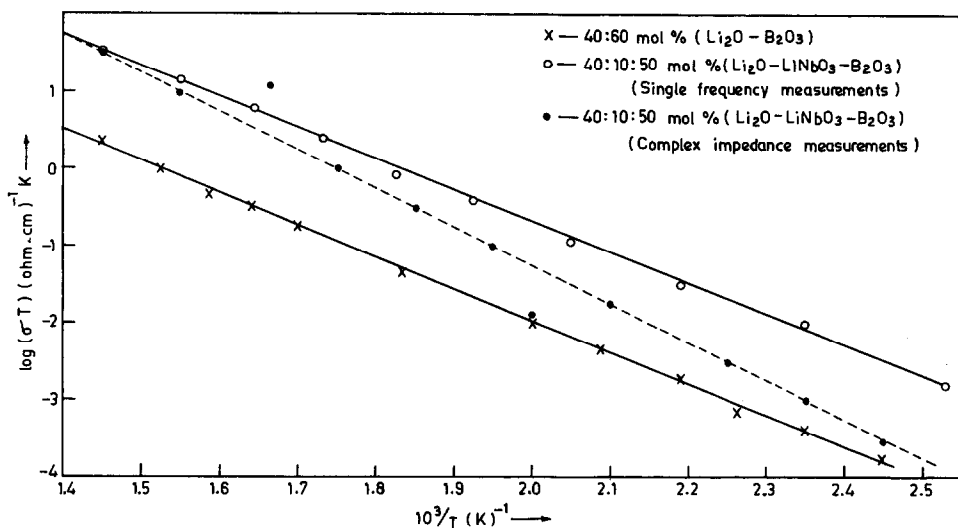


Fig. 2. Effect of LiNbO_3 addition on the electrical conductivity of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ (40:60 mole%) glass system.

TABLE 2

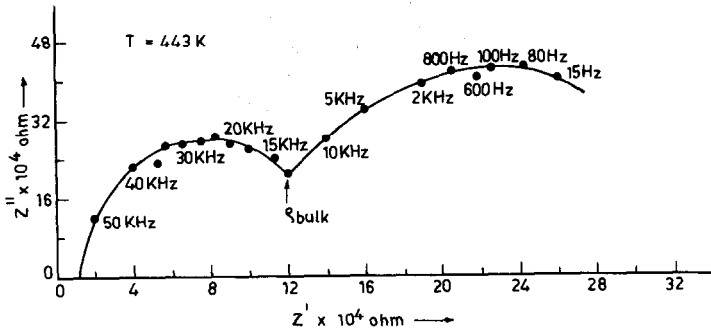
Comparison of conductivity values of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$ systems at 473 and 623 K

System	Conductivity $(\text{ohm cm})^{-1}$
$\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ 40:60 mol%	$\sigma_{(473 \text{ K})} = 6.38 \times 10^{-6}$ $\sigma_{(623 \text{ K})} = 1.15 \times 10^{-4}$
$\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$ 40:10:50 mol%	$\sigma_{(473 \text{ K})} = 1.43 \times 10^{-4}$ $\sigma_{(623 \text{ K})} = 1.43 \times 10^{-2}$ * $\sigma_{(473 \text{ K})} = 3.35 \times 10^{-5}$ * $\sigma_{(623 \text{ K})} = 9.03 \times 10^{-3}$

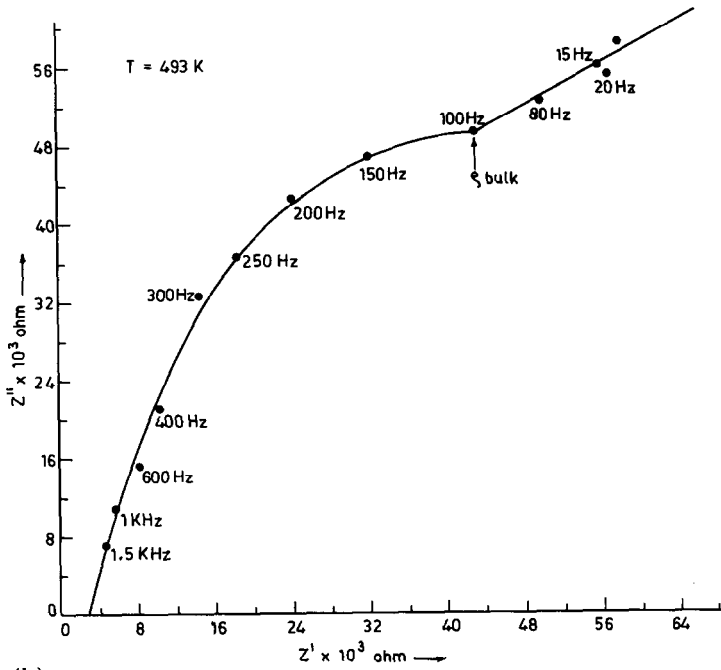
*Bulk conductivity calculated from complex impedance plots.

As the temperature increases, the 'bulk' semicircle moves to lower values of impedance and higher frequencies. Consequently, for the frequency range covered, only the electrode impedance is observed at higher temperature.

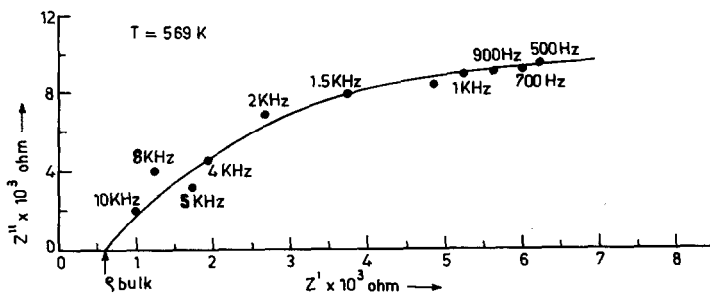
In Fig. 2, $\log(\sigma T)$ vs. $10^3/T$ (where σ is derived from complex impedance plots) for the LiNbO_3 -containing sample is also included. From the Figure it may be concluded that, at higher temperatures, single frequency data are reasonably consistent with the complex impedance results which are in agreement with already reported work on the lithium-borate glass system [15].



(a)

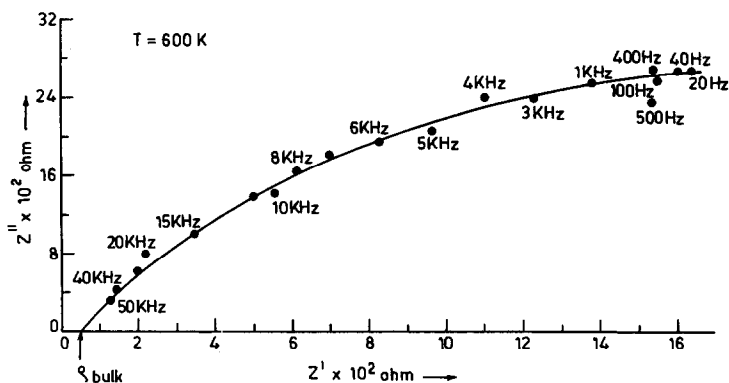


(b)



(c)

Fig. 3(a) - (c). For legend please see facing page.



(d)

Fig. 3. (a), (b), (c), (d) Complex impedance plots (Z' vs. Z'') for $\text{Li}_2\text{O-LiNbO}_3\text{-B}_2\text{O}_3$ (40:10:50 mole%) at four different temperatures. ρ_{bulk} gives the bulk resistivity at each temperature.

TABLE 3

Comparison of the conductivity values from the present investigation with earlier reports

Serial no.	System	Conductivity (ohm cm^{-1})	Reference
1	$\text{Li}_2\text{O-B}_2\text{O}_3$ 40:60 mol%	$\sigma_{(298 \text{ K})} = 7.1 \times 10^{-8}$ $\sigma_{(623 \text{ K})} = 6.1 \times 10^{-3}$	1
2	$\text{Li}_2\text{O-B}_2\text{O}_3$ 43:57 mol%	$\sigma_{(473 \text{ K})} = 2.95 \times 10^{-5}$	5
3	$\text{Li}_2\text{O-SiO}_2$ 40:60 mol%	$\sigma_{(373 \text{ K})} = 1 \times 10^{-6}$	2
4	$\text{Li}_2\text{O-SiO}_2$ 33.3:66.7 mol%	$\sigma_{(623 \text{ K})} = 1.9 \times 10^{-3}$	9, 20
5	$\text{Li}_2\text{O-Nb}_2\text{O}_5$ 50:50 mol%	$\sigma_{(623 \text{ K})} = 5.3 \times 10^{-3}$	13
6	$\text{LiNbO}_3\text{-SiO}_2$ 65:35 mol%	$\sigma_{(453 \text{ K})} = 1.0 \times 10^{-4}$	14
7	$\text{Li}_2\text{O-B}_2\text{O}_3$ 40:60 mol%	$\sigma_{(473 \text{ K})} = 6.38 \times 10^{-6}$ $\sigma_{(623 \text{ K})} = 6.84 \times 10^{-4}$	*
8	$\text{Li}_2\text{O-LiNbO}_3\text{-B}_2\text{O}_3$ 40:10:50 mol%	$\sigma_{(473 \text{ K})} = 1.43 \times 10^{-4}$ $\sigma_{(623 \text{ K})} = 1.43 \times 10^{-2}$	*

*Systems studied in present investigation.

Warburg type behaviour after passing through relaxation indicates a diffusion-controlled process in the electrolyte [19].

In Table 3, the conductivity values of the present investigation have been compared with those previously reported in the literature for implementing the material for practical application.

Conclusion

The $\text{Li}_2\text{O}-\text{LiNbO}_3-\text{B}_2\text{O}_3$ glass system has a high ionic conductivity (1.43×10^{-2} (ohm cm) $^{-1}$) at 623 K and may be suitable as an electrolyte material for an electrochemical power source.

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