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Effect of alumina on the structure and properties of $Li_2O–B_2O_3–P_2O_5$ glasses

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ABSTRACT

The structure of glasses within the system $Li_2O–Al_2O_3–B_2O_3–P_2O_5$ has been studied through ^{31}P, ^{11}B and ^{27}Al Nuclear Magnetic Resonance, and the effect of Al_2O_3 substitution by B_2O_3 and P_2O_5 network formers on the structure and properties investigated for a constant Li_2O content. Multinuclear NMR results reveal that substitution of Al_2O_3 for B_2O_3 and P_2O_5 network formers in a glass with composition $50Li_2O·15B_2O_3·35P_2O_5$ produces a change in boron environment from four-fold to three-fold coordination. Meanwhile aluminum can be present in four-, five- and six-fold coordinations a higher amount of Al(IV) groups is found for increasing alumina contents. The behavior of the glass transition temperature and electrical conductivity of the glasses has been interpreted as a function of the structural changes induced in the glass network when alumina is substituted for B_2O_3, P_2O_5 or both. Small additions of alumina produce a drastic increase in glass transition temperature, while it does not change for $[Al_2O_3]$ greater than 3 mol.%. However, the electrical conductivity shows very different behavior depending on the type of substitution; it can remain constant when B_2O_3 content decreases or sharply decrease when P_2O_5 is substituted by Al_2O_3, which is attributed to a higher amount of BO_3 and phase separation.

1. Introduction

Lithium phosphate glasses have gained a great attention during the last decades due to their interest in the development of solid electrolytes for energy devices [1], especially in the form of thin films for all-solid-state lithium rechargeable batteries [2]. Solid electrolytes present several advantages compared to liquid ones, such as being non contaminant, do not contain flammable organic compounds, and a separator is not needed to prevent physical contact between both anode and cathode electrodes. The main requirement that solid electrolytes must fulfill is to possess a high electrical conductivity, purely ionic, together with a suitable thermal and chemical stability within a wide electrochemical window, as well as to be compatible with the electrode materials. Amorphous materials based on lithium phosphates have demonstrated to be suitable for their application in lithium microbatteries, such as LiPON amorphous thin films [2], prepared through RF-magnetron sputtering of Li_3PO_4 under nitrogen atmosphere that present an electrical conductivity of $2 \cdot 10^{-6}$ S cm^{-1} at room temperature.

Phosphate glasses typically present low electrical conductivity and poor chemical stability; however, the introduction of secondary network formers, such as SiO_2 or B_2O_3, or intermediate, as Al_2O_3, allows an improvement of their properties. In lithium metaphosphate glasses, it has been observed that the introduction of aluminum oxide produces an increase in the electrical conductivity [3], due to the increased mobility of Li^+ cations by the formation of charge compensation pairs between Li^+ and the different aluminum coordination polyhedra, which also improves the chemical durability. Thus, the introduction of boron oxide, results in the increase in electrical conductivity as a consequence of the formation of $Li^+[BO_4]^-$ pairs [4–8]. The processing of amorphous thin films of the $Li_2O–P_2O_5$ [2] and $Li_2O–B_2O_3–P_2O_5$[9–11] systems throughout different methods, e.g. RF-magnetron sputtering or spray hydrolysis, has opened the opportunity to the application of these materials as all-solid electrolytes.

The structural changes induced by the substitution of aluminum or boron oxides for P_2O_5 in alkali phosphate glasses have been previously studied, showing that aluminum is present in three different coordination polyhedra, in four, five and six-fold coordination. When Al_2O_3 content increases the proportion of AlO_4 groups increases, thus increasing the former character of aluminum oxide [3,12,13]. However, when B_2O_3 enters in the structure, boron appears in three and four-fold coordination, the so-called BO_3 and BO_4 groups [14], and the increase in alkali oxide content produces the transformation of BO_3 groups into BO_4 ones, as observed in $Na_2O–B_2O_3–P_2O_5$ glasses [14].

In glasses of the $Na_2O–Al_2O_3–B_2O_3$ system [15], the competition of aluminum and boron by oxygen depends on the alkali content and the formation of AlO_4 tetrahedra is favored against that of BO_4 ones. On the other hand, in non alkali-containing phospho-aluminoborate glasses, it has been observed that increasing contents of P_2O_5 give rise to the formation of highly coordinated aluminum polyhedra, with

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high amounts of Al in five-fold coordination [16], and no Al/B connectivity detected. However, to the best of our knowledge, there are no reports on the structural speciation and properties of Li_2O–Al_2O_3–B_2O_3–P_2O_5 glasses. Therefore, the aim of this work has been the study of the distribution of the different structural arrangements in lithium-containing alumino-borophosphate glasses with a high content of lithium ions where a high ionic conductivity would be an important issue for their practical applicability as solid electrolyte materials. The structural characterization of glasses in the system Li_2O–Al_2O_3–B_2O_3–P_2O_5 has been carried out through multinuclear ^{31}P, ^{11}B and ^{27}Al Nuclear Magnetic Resonance, and the effect of alumina additions on the properties and, in particular, on the electrical conductivity of the glasses, has been followed through the structural, as well as microstructural, changes produced within the glass network.

2. Experimental

2.1. Preparation of the glasses

The studied glasses belong to the system Li_2O–Al_2O_3–B_2O_3–P_2O_5, for a constant lithium oxide content of 50 mol.%. Glasses were prepared by melt-quenching technique from batches of reagent grade materials: Li_2CO_3 (99% ACS. Reagent, Aldrich), $Al(PO_3)_3$ (Aldrich), $Li_2B_4O_7$ (99%, Panreac) and $(NH_4)_2HPO_4$ (99% ACS. Reagent, Merck). The batches were calcined in porcelain crucibles in an electric furnace up to 400 °C during 1 day, then melted during 2 h at temperatures ranging from 800 °C to 900 °C, depending on their composition. The glasses were obtained by pouring the melts onto brass plates. Glasses with alumina content higher than 5 mol.% were pressed between two steel plates to prevent spontaneous crystallization. Finally, glasses were annealed slightly above their glass transition temperature (T_g), previously determined by Differential Thermal Analysis (DTA). The glasses were transparent and X-ray Diffraction (XRD) patterns revealed that they were amorphous. Table 1 shows the glass composition, in mol.%, for the series $50Li_2O \cdot xAl_2O_3 \cdot (15-x/2)B_2O_3 \cdot (35-x/2)P_2O_5$, $50Li_2O \cdot xAl_2O_3 \cdot (15-x)B_2O_3 \cdot 35P_2O_5$ and $50Li_2O \cdot xAl_2O_3 \cdot 15B_2O_3 \cdot (35-x)P_2O_5$, where the B_2O_3/P_2O_5 ratio, P_2O_5 and B_2O_3 content have been kept constant, respectively.

2.2. Characterization of the glasses

MAS (Magic Angle Spinning) NMR (Nuclear Magnetic Resonance) spectra were recorded on a BRUKER 400 MHz spectrometer. ^{31}P MAS NMR spectra were recorded at 161.96 MHz with pulse length 4 μs, which corresponds to angle of 80°, and delay time of 40 s. A total number of 128 scans were accumulated with a spinning rate of 10 kHz. Solid $(NH_4)H_2PO_4$ (ADP) was used as secondary reference with a chemical shift 0.81 ppm with respect to H_3PO_4 (85%). ^{11}B NMR spectra were recorded at 128.38 MHz with 1 μs pulse length (15°) and 1 s delay time. A total number of 1024 scans were accumulated with a spinning rate of 10 kHz. A solution of $BF_3 \cdot Et_2O$ was used as primary reference. ^{27}Al MAS NMR spectra were recorded at 104.26 MHz (9.4T). The pulse length was 2.7 μs corresponding to angle of 30° and delay time was 2 s. A total number of 1024 scans were accumulated with a spinning rate of 10 kHz. Solid $Al(SO_4)_2(NH_4).12H_2O$ was used as secondary reference with chemical shift of −0.4 ppm with respect to $Al(NO_3)_3$ (0.1 M).

Glass transition temperature (T_g) has been determined by Differential Thermal Analysis (DTA) in a SEIKO–6300 ATD/TG analyzer, using platinum crucibles and a constant heating rate of 10 °C/min within the temperature range from 25 to 800 °C under air flow. Glass transition temperature is determined at the onset of the endothermic effect shown in the DTA patterns, and the error in T_g is taken to be within ±5 °C. The glass transition temperature for $50Li_2O \cdot 15B_2O_3 \cdot 35P_2O_5$, $50Li_2O \cdot 3Al_2O_3 \cdot 13.5B_2O_3 \cdot 33.5P_2O_5$ and $50Li_2O \cdot 5Al_2O_3 \cdot 12.5B_2O_3 \cdot 32.5P_2O_5$ glasses was also determined by dilatometry in a Netzsch Gerätebau dilatometer, model 402 EP, using a 10 K min^{-1} heating rate in air. The estimated error of T_g is ±2 °C, being ΔT_g (ATD) > ΔT_g (dil).

X-ray diffraction (XRD) patters were obtained on a powder diffractometer Bruker D-8 using monochromatic Cu Kα radiation ($\lambda = 1.540598$) for 2θ from 10 to 70°.

Electrical conductivity measurements were performed by Electrochemical Impedance Spectroscopy in a GAMRY REF600 impedance analyzer, in the frequency range from 10 Hz to 1 MHz at temperatures between 25 and 130 °C. The samples were cut into cylinders, approximately 8 mm in diameter and 1–2 mm thick, and their faces were polished with P600 grit SiC paper. The electrodes were obtained by painting both faces with silver paste (Silver conductive paint, Electrotube®). Nyquist plots of complex versus real impedance components have been fitted to an equivalent circuit composed of a capacitor (C_1) in parallel with a resistance R_1 and a Warburg impedance (W), representing the electrode phenomena occurring between the surface sample and the electrodes, in series with a resistance (R_2) and a parallel capacitance (C_2) representing the conductivity and dielectric properties of the bulk sample. The electrical conductivity (σ) is determined, for each temperature, through the resistance value (R_2) read at the low frequency intersection of the semicircle with the x-axis in the Nyquist plots using the sample geometric factor (e/A; e = thickness, A = electrode area) in the equation:

$$\sigma = (1/R_2).(e/A) \quad (1)$$

Phase separation phenomena were studied through Transmission Electronic Microscopy (TEM), which was performed in a Hitachi H-7100 (125 kV) microscope. Samples were chemically etched with 2 vol. % HF.

Table 1
Nominal composition of lithium alumino-borophosphate glasses.

Glasses	Li_2O	Al_2O_3	B_2O_3	P_2O_5
$50Li_2O \cdot xAl_2O_3 \cdot (15-x/2)B_2O_3 \cdot (35-x/2)P_2O_5$ (x = 3, 5, 7, 10)				
3Al (BP)	50.0	3.0	13.5	33.5
5Al (BP)	50.0	5.0	12.5	32.5
7Al (BP)	50.0	7.0	11.5	31.5
10Al (BP)	50.0	10.0	10.0	30.0
$50Li_2O \cdot xAl_2O_3 \cdot 15B_2O_3 \cdot (35-x)P_2O_5$ (x = 3, 5, 7, 10)				
3AlP (B)	50.0	3.0	15.0	32.0
5AlP (B)	50.0	5.0	15.0	30.0
7AlP (B)	50.0	7.0	15.0	28.0
10AlP (B)	50.0	10.0	15.0	25.0
$50Li_2O \cdot xAl_2O_3 \cdot (15-x)B_2O_3 \cdot 35P_2O_5$ (x = 3, 5, 7, 10)				
3AlB (P)	50.0	3.0	12.0	35.0
5AlB (P)	50.0	5.0	10.0	35.0
7AlB (P)	50.0	7.0	8.0	35.0
10AlB (P)	50.0	10.0	5.0	35.0

3. Results

3.1. Structure and microstructure of glasses

Fig. 1 shows the ^{31}P, ^{11}B and ^{27}Al MAS NMR spectra of glasses with composition $50Li_2O \cdot xAl_2O_3 \cdot (15-x/2)B_2O_3 \cdot (35-x/2)P_2O_5$ (x = 3, 5, 7, 10 mol.%), where B_2O_3/P_2O_5 ratio remains constant. ^{31}P MAS NMR spectra (Fig. 1a) show a broad resonance comprised between −20 and −5 ppm, which can be decomposed in several individual resonances. Besides, the spectra also present a much less intense resonance at 10 ppm, corresponding to orthophosphate groups, or Q^0