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Structure, thermal analysis and optical properties of lithium tungsten-titanophosphate glasses

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ABSTRACT

A melt-quenching method is used to prepare homogeneous glasses inside the $20Li_2O$-(50-x)Li_2WO_4-xTiO_2-$30P_2O_5$ (x = 0, 5, 8, 10 and 15 mol%) system. The amorphous and glassy states of the glasses are evidenced by the X-ray diffraction and differential scanning calorimetry (DSC) analysis, respectively. The glasses were found to be colorless. The determined parameters for the glasses such as density, molar volume and glass transition temperature (T_g) depend strongly on the chemical composition of the glasses. The density and T_g are found to decrease and increase with TiO_2 content, respectively. Infrared (IR) spectroscopy is used to characterize their structural approach. This technique has allowed the identification of different phosphate structural units mainly pyrophosphate and metaphosphate in their structure. From the absorption edge studies, the values of the optical band gap, E_g, and Urbach energy, ΔE, were evaluated. The optical band gap is found to depend on the glass composition and it decreases as the content of the TiO_2 increases.

1. Introduction

Phosphate glasses have received considerable attention in the past few years due to the synthesis of new glass compositions with high chemical stability. The improvement of chemical stability [1–3] stimulated the application of phosphate glasses in several fields of materials science, such as fast ionic conductors, semiconductors, photonic materials [4], hermetic seals [5], rare-earth ion host solid state lasers [6] and biomedical materials [7]. Phosphate glasses have also drawn much attention as promising candidates for low melting glasses, because they exhibit low glass transition temperature, appropriate thermal expansion coefficient and low viscosity [8]. The structure of these glasses consist of PO_4 tetrahedra, which can be attached to a maximum of three neighboring tetrahedra forming a three dimensional network as in vitreous P_2O_5. The addition of oxide modifier to the glass former P_2O_5 leads to a depolymerisation of the network, with the breaking of P—O—P linkages and the creation of non-bridging oxygen. The modifying cations can provide ionic cross-linking between the non-bridging oxygen of two phosphate chains, thus increasing the bond strength of this ionic cross-link and improving the mechanical strength and chemical durability of the glasses [1]. For instance, the addition of TiO_2 or WO_3 to phosphate glasses improves their chemical durability, thermal stability and other physical properties [9–11]. These changes are due to the incorporation of TiO_x or WO_x structural units into the phosphate structural network, which is accompanied by the formation of M—O—P and M—O—M bonds (M═Ti, W) [10,12]. Moreover, when P_2O_5 oxide former is mixed with materials with high linear refractive indices, such as WO_3 and TiO_2, the glasses possess high linear and nonlinear refractive indices, and semiconducting properties [13]. Nonlinear optical titanophosphate glasses related to distortions of Ti-polyhedra are widely investigated for future photonics applications because of fast response time, high transparency, isotropy and good compatibility with waveguide and fiber fabrication [14]. It is reported that TiO_2-containing glasses in the system of R_2O–TiO_2–P_2O_5 (R = Li, Na, K) present non-linear optic index and the thermo-optic effect [15]. The study of Li_2O–TiO_2–P_2O_5 glasses revealed that replacement of P_2O_5 by TiO_2 leads to significant changes in the physico-chemical and thermal properties of these glasses. DTA and electrical conductivity measurements showed that the incorporation of TiO_2 into the structural network of the lithium phosphate glasses results in an increase of the glass transition temperature and the electrical conductivity [16].

Tungsten oxide based materials are well known for their electrochromic, photochromic properties and a wide range of other practical applications [17]. Photochromic materials are very interesting because of their potential applications in memory and display devices [18]. Recently, it is reported that tungsten phosphate glasses presented photochromism in a wide range of wavelengths [19]. More recently,

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W. Shen et al. [20] studied the photochromic behaviors of WO_3-P_2O_5 glasses and concluded that it corresponded to the conversion of W^{6+} to W^{5+} or W^{4+} as well as to the existence of WO_6 clusters in the structure of the glasses. The existence of tungsten in different valence states is expected to have profound influence on physical properties of lithium phosphate glasses. For instance, it is suggested that oxide glasses that contain transition-metal ions often exhibit electronic conductivity when the transition-metal ions are present in more than one valence state. The electronic conduction is fundamentally caused by electron transfer between the transition-metal ions in different valence states [21]. However, the relative number of reduced ions is typically small unless the glasses are prepared under controlled conditions, such as the introduction of reducing agents into the melt or the use of a strongly reducing atmosphere.

Lithium phosphate glasses are well known due to their variety of technological applications like solid electrolytes in electrochemical devices [22]. The key property of a glass electrolyte is very low electronic conductivity and sufficiently high lithium transport properties. To achieve high ionic conductivity, the electrolytes must contain a high concentration of-type of mobile cations. Thus, in our previous study [23], we have studied highly modified glasses inside the Li_2O-Li_2WO_4-P_2O_5 system and found that the colorless glasses are transparent and contained tungsten only as W^{6+} ions. Since the interest in lithium phosphate glasses which contain transition metals got intensified as they have been shown to be promising glassy electrolytes for the development of technologically and biologically important materials, we have focus our interest to study new glassy materials containing both TiO_2 and Li_2WO_4.

According to the above literature reports, the properties of phosphate glasses were correlated with the specific glass network formed in these glasses and TiO_2 or WO_3 is inserted inside the phosphate covalent network to form strong P—O—M bonds (M═Ti, W) and enhance the network connectivity. At high TiO_2 and WO_3 contents, MO_6 and MO_4 units link together through M—O—M bonds which were pointed out to be responsible of several of their properties. Thus, their thermal and durability properties should be further enhanced by the presence of both tungsten and titanium in the structure of the glasses. However, according to our knowledge, investigation of the glasses containing both tungsten and titanium are very few. Moreover, if the glasses contain high content of lithium they could show high electrical conductivity allowing them to be applied in several electrochemical devices. For these reasons, high lithium content glasses inside the system Li_2O-Li_2WO_4-TiO_2-P_2O_5 are studied.

The general aim to synthesis of the glasses is to understand some physical and structural aspects such as the connection mode of metal oxide units with PO_4 groups and the type of chemical bonds which appear in $20Li_2O$-(50-x)Li_2WO_4-xTiO_2-$30P_2O_5$ glasses. Specially, in this work we will study the effect of the substitution of Li_2WO_4 by TiO_2 on the structure, thermal and chemical properties of these glasses.

2. Experimental procedure

$20Li_2O$-(50-x)Li_2WO_4-xFe_2O_3-$30P_2O_5$ glasses were prepared from lithium carbonate (Li_2CO_3), titanium trioxide (TiO_2), lithium tungstate Li_2WO_4, and hydrogen ammonium phosphate ($NH_4H_2PO_4$) purchased from Aldrich Chemicals. These precursors were weighed in a microanalytical balance and mixed thoroughly according to appropriate molar compositions. The mixture was first heated at 300 °C and 600 °C for several hours in an alumina crucible placed in an electric furnace. The first treatment served to remove water and ammonia in $NH_4H_2PO_4$ so as to prevent the excess boiling and consequent spillage. The second heat treatment at 600 °C for 6 h allowed the decomposition of the carbonates. Then, the temperature of the furnace is increased to attain the melt and was stirred for homogenization for about 30 min at 900 °C, the preparation temperature. The melt was then quenched to room temperature in air by pouring it on a preheated aluminum polished plate and pressing quickly by another one. The thin disks of glasses obtained in the above manner were transparent and colorless. Care was taken to see that the samples were not exposed to moisture, so they were placed in a desiccator before uses.

The amorphous state of all as-quenched samples was confirmed by powder X-ray diffractometry (XRD), using a Phillips D5000 apparatus equipped with a CuK_α X-ray source and a Ni filter ($\lambda = 1.54$ Å). No Bragg peaks were detected in a wide range of 2θ angles between 10° and 80°.

The density measurements (ρ) of glasses are determined by the Archimedes method using diethyl orthophthalate at 22 °C as the suspension medium. The uncertainty of the measurements is estimated to be ± 0.01 g/cm^3. Molar volume (V_m) of each glass is derived from the molar weight values (M) and the density ($V_m = M/\rho$).

The thermal stability of the studied glasses was studied by the Differential Scanning Calorimetry (DSC). DSC curves were carried out for ground glass batches of about 130 mg in nitrogen atmosphere at a heating rate 10 °C/min using DSC131 Evo analyzer. The estimated error on the temperature is ± 4 °C. Since the particle size of the ground glass batches can affect the shape of the DSC curves, we have used nearly the same particle sizes (glass powder passed through a 500 μm sieve but was retained over a 300 μm sieve) in all the determinations.

The local structure of the samples was examined by the Fourier transform infra-red FTIR TENSOR27 spectrometer. FTIR absorption spectra of all glasses were recorded in the 400–1500 cm^{-1} frequency range at room temperature. For these measurements, each sample was ground to a fine powder, mixed with KBr in the ratio 1:300, and vacuum pressed into a disk.

UV–vis diffuse reflectance spectroscopy was performed on a Jasco v-570 spectrophotometer over the spectral range of 200–800 nm. A barium sulfate ($BaSO_4$) plate was used as the standard (100% reflectance) on which the finely ground sample from the glass was coated.

3. Results and discussion

3.1. Glassy formation and XRD analysis

The experimental procedure described above has allowed the preparation of homogeneous glasses. The series of glasses $20Li_2O$-(50-x)Li_2WO_4-xTiO_2-$30P_2O_5$ (x = 0, 5, 8, 10, 15 mol%) offers fixed content of phosphate. The samples inside the system $20Li_2O$-(50-x)Li_2WO_4-xTiO_2-$30P_2O_5$ (x = 0, 5, 8, 10, 15 mol%) prepared by the conventional melt-quenching route were free from visible inhomogeneities, such as inclusions, cracks or bubbles. The homogeneous samples could be elaborated up to 15 mol% of TiO_2. The structural nature of the elaborated samples is checked by X-ray diffraction analysis. XRD patterns for different samples (Fig. 1) show only broad humps at low angles instead of

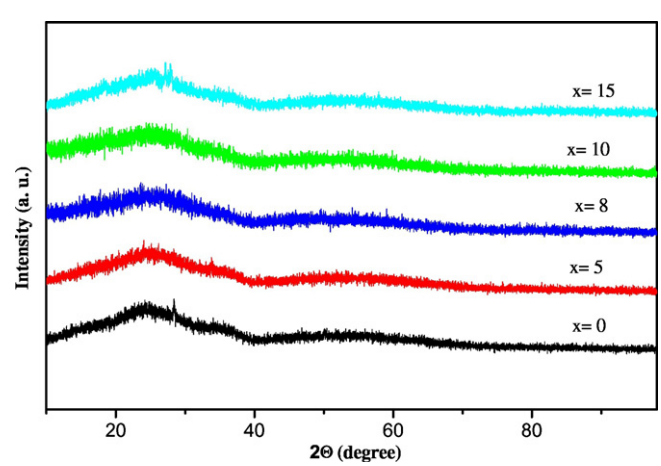

Fig. 1. X-ray patterns of the Li_2O-Li_2OWO_4-TiO_2-P_2O_5 glasses.