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Structural and thermal characterization of phosphate based glasses promising for hydrogen absorption

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ABSTRACT

Among the applications of phosphate glasses, one of the most promising is their potential as catalysts for water dissociation into hydrogen and oxygen and to absorb hydrogen in its structure, making them good candidates to be used as electrolytes in intermediate temperature fuel cells (200–500 °C). Phosphate based glasses with molar composition $30PO_{5/2}–25NbO_{5/2}–10WO_3–25Na_2O–10[(1-x)BaO–xSrO]$, with x = 0, 20, 50, 60, 80 and 100 mol% were prepared by the melt quenching technique. The as-prepared samples revealed to be transparent, mechanical and thermally stable at room temperature. Differential thermal analysis (DTA) measurements showed Tg values around 500 °C, and high thermal stability. The structure of the samples was studied by X-Ray powder Diffraction (XRD) Raman spectroscopy, and the morphology by Scanning Electron Microscopy (SEM). Dc (σ_{dc}) and ac (σ_{ac}) conductivities and dielectric spectroscopy measurements were performed as function of temperature (100–370 K) presenting a conductivity predominantly ionic ($\sigma_{electronic}/\sigma_{ionic}$ of about 10^{-4}). The dielectric spectroscopy was measured in the frequency range 100 Hz–1 MHz.

1. Introduction

Hydrogen based energy systems are defined to be one of the technological solutions for reducing emission of greenhouse gases. There is a great interest on developing techniques for hydrogen production, safe and reliable storage and delivery, preferably, using clean or renewable energies for the conversion of the chemical energy of hydrogen to electricity and/or heat. One of the topics of greatest interest in this area is the development of new highly efficient catalysts and electrolytes for fuel cells. Currently, proton-conducting polymer electrolyte membrane fuel cells are used for temperatures below 100 °C and solid oxide fuel cells for temperatures between 800 and 1000 °C [1]. Intermediate temperature fuel cells remains a subject under improvement, since new materials able to be efficiently used as electrolytes between temperatures of 200 and 500 °C are still needed. Glass materials are stable in this range of temperatures and can have an open structure with no grain boundaries, which makes them good candidates for this application [2].

Among glass materials, phosphate glasses are promising as new solid-state electrolytes because their structure allows a high mobility for protons [3]. Protonic and electronic mixed conductors have been expected as hydrogen separation membrane materials because of their high selectivity and permeability of hydrogen. The structure of these glasses can be described as a network of PO_4 structural units linked through covalent bonding of corner shared oxygen atoms, referred to as bridging oxygen atoms (BOs) [4,5]. The addition of network modifying oxides in the glass, leads to the depolymerization of the phosphate chains build by P–BO–P bonds, and subsequent formation of non-bridging oxygen ions (NBOs) [4,5]. Therefore, the linked phosphate tetrahedra can have three, two, one or none bridging oxygen ions. The various types of phosphate tetrahedra that result from this classification are labeled using the Q^n terminology, where n represents the number of BOs per PO_4 tetrahedron [4,5]. The isolated PO_4 tetrahedra Q^0 are named orthophosphate, Q^1 pyrophosphate, Q^2 metaphosphate and the Q^3 groups with three bridging and one terminal oxygen (P = O bond) are named ultraphosphate [4,5].

According to some studies [2,6], phosphate glasses containing tungsten oxide, which is an incipient glass network former, decompose water vapor and absorb hydrogen. Tungsten phosphate glasses react with hydrogen and water vapor at the ambient temperatures below the glass transition temperature (Tg) and W^{6+} ions in the glasses are reduced to W^{5+}. Hydrogen generation on these glasses is associated with a redox pair of proton and electron trapped on W^{6+}. On other words, water vapor is dissociated at the surface of the glasses and the generated hydrogen is selectively dissolved into the glass by donating an electron to W^{6+} ions in the temperature range of 300–550 °C. The absorption of the H^+ happens when the proton diffuses to the glass structure and bonds with the non-bridging oxygen ions in the matrix.

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Another interesting work describing phosphate glasses as good proton conductors was reported by T. Ishiyama et al. [1,7]. The authors successfully developed a technique to inject hydrogen protons into sodium phosphate glasses by an electrochemical substitution of the alkali ions with protons. They stated that when the substitution is performed in a hydrogen containing atmosphere between 300 and 500 °C, the hydrogen protons injected into the glass structure are stably sustained at this range of temperatures. This technique could be an additional procedure to increase the proton concentration on this kind of glasses and to improve their capability to be used as intermediate temperature fuel cells.

Therefore, the study of new phosphate glass systems thermally stable at temperatures between 200 and 500 °C, with reduced electronic conductivity and with a large number of non-bridging oxygen in their structure, is a topic of extensive consideration. The improvement of the chemical stability also stimulates the employment of these glasses in applications such as fast ionic conductors, photonic materials and rare-earth ion host solid state lasers [8,9]. Furthermore, niobium phosphate glasses might have potential to be used as glass fibers, optical lenses, hermetic sealing and electrodes [8,9].

In the present work, glasses with molar composition $30PO_{5/2}$–$25NbO_{5/2}$–$10WO_3$–$25Na_2O$–10[(1-x)BaO–xSrO], with x = (0, 20, 50, 60, 80, 100) were prepared by the melt quenching technique. To promote electronic conduction, niobium and tungsten oxides were included in the glass composition. The presence of sodium ions will contribute to the ionic conductivity and therefore a mixed-conduction effect (electronic and ionic) is expected. The introduction of the alkali-earth ions is mainly related with the known increasement of the chemical durability of these phosphate based glasses [10]. However, knowing that the O–H bonding strength in phosphate glasses is dependent on the type of alkali-earth ion, thus having an influence on the proton conduction behavior [3], the substitution of barium ions by strontium was made and the consequent effect analyzed by X-Ray diffraction, differential thermal analysis, Raman spectroscopy and scanning electron microscopy. Electrical conductivity and dielectric spectroscopy measurements were related to the sample microstructural properties.

2. Experimental details

2.1. Sample preparation

Functional glasses with molar composition $30PO_{5/2}$–$25NbO_{5/2}$–$10WO_3$–$25Na_2O$–10[(1-x)BaO–xSrO], with x = 0, 20, 50, 60, 80 and 100 mol% were prepared by the melt quenching technique, using high purity chemicals (>99%) P_2O_5, Nb_2O_5, WO_3, Na_2CO_3, $SrCO_3$ and $BaCO_3$ in powder form. The reagents, in the appropriate amounts were mixed for 30 min in a Fritsch Pulverisette 5 agate ball-mixing planetary system, in order to improve the homogeneity of the mixtures. Afterwards, the mixtures were melted at 1350 °C in alumina crucibles with a closed lid, for about 15 min. After 7 min at 1350 °C, and for each composition, the crucible was manually stirred in order to homogenize the melt. The melts were poured into a stainless steel slab which was immediately introduced in a second furnace pre-heated at 300 °C. The samples were then maintained at 300 °C for about 12 h, to improve the glasses mechanical stability by relieving internal stresses. All compositions resulted in transparent glasses, and the samples with higher strontium content displayed a slightly yellow coloration. The samples identification and the respective molar composition are indicated in the Table 1.

2.2. Structural and morphological characterization

The X-Ray Diffraction patterns (XRD) were obtained at room temperature on an Philips X'Pert MPD difractometer (CuKα radiation, λ = 1.54056 Å) operating at 45 kV, and 40 mA, with a curved graphite monochromator, an automatic divergence slit, a progressive receiving slit and a flat plane sample holder in a Bragg-Brentano parafocusing configuration. A scan step of 0.02° in 1 s in the 2θ angle range of 10–60° were the measurement parameters. Room temperature Raman spectroscopy was carried out in a Jobin Yvon HR 800 spectrometer, using the excitation line of 532 nm. The spectra were obtained in a back-scattering geometry, between 100 and 1200 cm^{-1}.

Table 1
Molar composition of the prepared glasses.

	Molar composition (%)					
	P_2O_5	Nb_2O_5	WO_3	Na_2O	BaO	SrO
Glass Sr-0	20.7	17.2	13.8	34.5	13.8	0.0
Glass Sr-20	20.7	17.2	13.8	34.5	11.0	2.8
Glass Sr-50	20.7	17.2	13.8	34.5	6.9	6.9
Glass Sr-60	20.7	17.2	13.8	34.5	5.5	8.3
Glass Sr-80	20.7	17.2	13.8	34.5	2.8	11.0
Glass Sr-100	20.7	17.2	13.8	34.5	0.0	13.8

The morphology of the glasses was observed by Scanning Electron Microscopy (SEM), performed in a Hitachi S4100-1 system, on the free surface of the glasses. All samples were covered with carbon before microscopic observation.

2.3. Differential thermal analysis

The glass transition temperature (Tg) and crystallization temperature (Tc) of the samples were determined by differential thermal analysis (DTA), on a Linseis apparatus, at the rate of 10 °C/min.

2.4. Electrical and dielectric measurements

For the electrical measurements the sample surfaces were polished before the heat treatments until a thickness of about one millimeter and parallel faces were achieved. The electrodes were formed by painting both sides of the samples surfaces with silver conductive paste. With this geometry, it is valid to consider the samples as parallel plate capacitors, and consequently to apply well known equations in order to calculate the complex permittivity [11,12].

The dc electrical conductivity (σ_{dc}) of the samples was measured with a Keithley 617 electrometer, capable of measuring currents down to 10^{-14} A. This measurement was performed in a temperature range between 100 and 370 K, using a nitrogen bath cryostat setup. During the measurements, the samples were kept in a helium atmosphere to minimize thermal gradients. The ac electrical conductivity (σ_{ac}) and impedance measurements were performed in the temperature range of 200 to 370 K, using the same bath cryostat, with a Network Analyzer, Agilent 4294, operating between 100 Hz and 1 MHz in the C_p–R_p configuration (capacitance in parallel with resistance). In both measurements, dc and ac, the temperature of the samples was controlled by an Oxford Research IT-C4 and measured using a platinum sensor. In both dc and ac, the activation energy (E_a) was calculated for the high temperature range, by fitting the data according with Arrhenius model (Eq. (1)) [13–15]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{1}$$

where σ_0 is a pre-exponential factor, E_a the activation energy, k_B the Boltzmann constant and T the temperature. E_a can be calculated from the slope of $\ln(\sigma_{dc})$ versus 1/T.

The impedance spectroscopy measurements were performed in the frequency range of 100 Hz–1 MHz. The real and complex parts of the permittivity were calculated using the relations (2) and (3) [13,14]:

$$\varepsilon' = \frac{d}{A}\frac{C_p}{\varepsilon_0} \tag{2}$$