Journal of Non-Crystalline Solids 473 (2017) 114–119

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Influence of melting conditions on the water content and structure of K_2O-La_2O_3-Al_2O_3-SiO_2-P_2O_5 glasses

Francisco Muñoz[a,*], Pedro Moreno-Zárate[b], Javier Solís[c]

[a] Institute of Ceramics and Glass (CSIC), Kelsen 5, 28049 Madrid, Spain
[b] Industrial Engineering School, Tepexi Higher Technological Institute, Av. Tecnológico S/N, 74690 Tepexi de Rodríguez, Mexico
[c] Laser Processing Group, Institute of Optics (CSIC), Serrano 121, 28006 Madrid, Spain

ARTICLE INFO

Keywords:
Phosphate glasses
Structure
Water
NMR
Femtosecond laser writing

ABSTRACT

Glasses of the system of composition K_2O-La_2O_3-Al_2O_3-SiO_2-P_2O_5 have recently gained attention due to their response to femtosecond (fs) laser irradiation, and the fact that high repetition rate fs-laser writing allows for the production of very efficient waveguides. When doped with rare-earth ions, the glasses can also be used in amplifiers or lasers and, in this respect, a control of the water content in the phosphate-based glasses is of very high importance. Thus, in the present work we have studied the influence of the melting conditions on the final water content of glasses of the above system and on their structure as studied by Raman and Nuclear Magnetic Resonance spectroscopies. Increasing temperature and melting times conducts to the enrichment in SiO_2 and a depletion of K_2O and P_2O_5 contents in parallel with a reduction of the water content as measured by FTIR. On the other hand, the structural study showed that the chemical environment of phosphorous and silicon are not much affected by the changes in composition and that aluminium moves from being 6-fold coordinated to 4-fold. Finally, it has also been observed that SiO_2 enters in the glasses as fully polymerized, which is consistent with the reduction of water directly on the ratio between oxygen and phosphorus in the glasses.

1. Introduction

The presence of water in the form of OH (hydroxyl) ions is well known in phosphate glasses [1], and its influence can be very critical for certain phenomena such as luminescence of rare-earth doped glasses, causing quenching effects as well as crack growth during operation [2,3]. When doped with rare-earth elements, phosphate glasses may possess large emission cross sections and low non-linear refractive indices, thus being ideal for their application as solid state matrices for stimulated emission of light. Furthermore, to be suitable as laser hosts, the refractive index change across the glass must be $< 2 \times 10^{-6}$ and the absorption coefficient of the OH groups reduced to $< 5\ \mathrm{cm}^{-1}$ [4].

Increasing the melting time and temperature generally leads to a decrease of the water content in the glasses. An additional alternative is the use of dehydration agents, such as fluoride compounds or CCl_4 that are added to the batch. However, one of the most effective methods is oxygen bubbling directly throughout the melt [5].

Melting of phosphate glasses does also imply another issue concerning the calcination of the batches of raw materials that are known to easily produce corrosion of platinum crucibles [6]. However, a drawback when using long melting times in platinum crucibles is that inclusions of metallic Pt are very frequent and so their dissolution by oxidation is a required step during the fining process, which is usually done by O_2 bubbling through the melt. Thus, the preparation of neodymium phosphate laser glasses, for instance, is usually performed in a two-step melting procedure, first using a ceramic crucible, e.g. SiO_2, and then platinum for fining and homogenizing of the melt [7]. If large amount of silica is dissolved into the phosphate melts the glass properties may drastically change but, on the other hand, the formulation of SiO_2-containing phosphate or alumino-phosphate glasses gives rise to an improvement of the chemical, thermo-mechanical as well as luminescence properties, as it has been demonstrated for instance in Yb-doped alumino-phospho-silicate glasses [8].

Among phosphate glasses, the system of composition K_2O-La_2O_3-Al_2O_3-SiO_2-P_2O_5 has recently received particular attention due to their response to femtosecond (fs) laser irradiation, showing strong element redistribution in the laser-affected region. Although element redistribution has been observed upon sub-surface, fs-laser irradiation in a variety glasses, mostly silica-based [9], only recently evidence of local compositional changes leading to the production of highly efficient light guiding has been demonstrated [10]. High repetition rate fs-laser writing in these glasses leads to production of very efficient waveguides

---

* Corresponding author at: Instituto de Cerámica y Vidrio (CSIC), Kelsen 5, 28049 Madrid, Spain.
E-mail address: fmunoz@icv.csic.es (F. Muñoz).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.08.002
Received 15 June 2017; Received in revised form 1 August 2017; Accepted 2 August 2017

Table 1
Conditions of melting for each glass, values of nominal composition and analysed composition (in mol %), content of water in ppm and glass transition temperature of the four studied glasses.

Glass	Melting conditions	Analysed oxide content (mol %)					T_g (± 2 °C)	$[H_2O]$ (ppm)
		K_2O	Al_2O_3	SiO_2	La_2O_3	P_2O_5		
Nominal glass composition		8.5	9.1	–	9.1	73.3		
LAP1	1st: 1350 °C for 1 h in air	7.7	12.5	10.5	10.5	58.7	553	137.4
LAP2	1st: 1450 °C for 1 h in air 2nd: 1450 °C for 1 h in air	6.2	14.2	14.7	9.9	55.0	562	95.1
LAP3	1st: 1450 °C for 1 h in air 2nd: 1450 °C for 2 h in Ar 3rd: 1450 °C for 2 h in Ar	4.9	14.5	20.0	10.1	50.9	574	61.8
LAP4	1st: 1450 °C for 2 h in Ar 2nd: 1500 °C for 4 h in Ar	3.4	12.9	28.2	10.1	45.4	587	41.1

in a highly controllable manner [11]. The refractive index contrast of the waveguides is due to the cross migration of La and K ions leading to an enrichment of La_2O_3 in the guiding region, inducing index contrast values, $\Delta n > 10^{-2}$. This enables the production of strong confinement, light guiding structures. Recently, it has been demonstrated that this fs-laser induced ion migration process can be used for producing high efficiency waveguide amplifiers and lasers [12].

The presence of water in the pre-processed glass and how it is influenced by the glass preparation method is thus an important issue for this application. Therefore, the aim of this work was to investigate the effect of melting phosphate glasses in ceramic crucibles onto the composition, water content and the structure of the glass network. We prepared glasses of the system K_2O-La_2O_3-Al_2O_3-SiO_2-P_2O_5 following different routes in air and Ar atmosphere, and analysed their water content by FTIR spectroscopy and studied their structure through Nuclear Magnetic Resonance spectroscopy.

2. Experimental

The glasses were obtained by the melt-quenching method, then annealed at their glass transition temperature for 1 h. Initial batches for 50 g of glass with composition $8.5K_2O$-$9.1La_2O_3$-$9.1Al_2O_3$-$73.3P_2O_5$ (mol %) were prepared from reagent K_2CO_3 (Scharlau), La_2O_3 (99.9%, Sigma-Aldrich) and $(NH_4)_2HPO_4$ (Scharlau) raw materials. The batches were calcined slowly up to 400 °C overnight in porcelain crucibles (Haldenwanger 79MF 1a), then submitted to between 1 and 3 consecutive melting steps, at temperatures ranging between 1350 and 1500 °C and for different time lengths, either in air or argon flow depending on the melting conditions in each case. In each case, the obtained glasses were poured onto brass moulds, crushed and ground before being submitted to the subsequent melting step to obtain each final glass, which is finally annealed at the glass transition temperature.

The glass transition temperature (T_g) has been determined by Differential Thermal Analysis (DTA) in a SEIKO 6300 ATD/TG analyser, using platinum crucibles and a constant heating rate of $10\ °C \cdot min^{-1}$ within the temperature range from 25 to 800 °C under air. Glass transition temperature was determined at the onset of the endothermic effect shown in the DTA patterns with incertitude of ca. ± 2 °C.

Fourier Transformed Infrared (FT-IR) spectroscopy was performed on mirror-like polished glass samples of about 2 mm thick in a PerkinElmer Spectrum 100 spectrometer operating in the transmission mode within the wave number range of 450 to $5000\ cm^{-1}$. The coefficient of absorption of hydroxyl ions in the glasses (α_{OH}) was calculated using Eq. (1), according to the procedure described in [13], with respect to the maximum transmitted intensity at $5000\ cm^{-1}$:

$$\alpha_{OH} = -\lg(T_{3000}/T_{5000})/t \qquad (1)$$

where T_{3000} and T_{5000} are the transmission at 3000 and $5000\ cm^{-1}$, respectively, and t the sample thickness (in cm). In order to determine the actual OH^- concentration, the extinction coefficient of H_2O within the specific glass matrix is required and for the case of phosphates; typical values of the water extinction coefficient are of ca. $30\ ppm \cdot cm^{-1}$ [5].

X-Ray Fluorescence Spectroscopy was used to analyse the chemical composition of the obtained final glasses in a PANalytical MagicX 2400 spectrometer through the pearl method of 0.3 g of glass with 5.5 g of $Li_2B_4O_7$.

Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) was performed in a Bruker ASX 400 spectrometer. ^{31}P MAS NMR spectroscopy was performed at 161.96 MHz (9.4 T). A π/6 and 40 kHz pulse was used with recycle delay of 60 s. A total number of 64 scans were accumulated with a spinning rate of 10 kHz. Solid $(NH_4)H_2PO_4$ was used as secondary reference with a chemical shift of 0.81 ppm with respect to H_3PO_4 (85%). The ^{27}Al MAS NMR spectra were obtained at 105.9 MHz. A π/30 pulse with length of 0.4 μs, 2 s recycle delay, 2048 scans, and 10 kHz spinning frequency were employed. ^{27}Al MAS NMR spectra were simulated using Czjcek model [14] with dmfit software [15]. The ^{29}Si MAS NMR was obtained at 79.49 MHz, with a π/2 pulse of 50 kHz, 60 s recycle delay and 40 kHz spectral window for overnight accumulation. Kaolinite served as secondary reference with a chemical shift of − 91.2 ppm respecting to TMS. All recycling delays between acquisitions were performed sufficiently long as to ensure full relaxation and provide reliable quantification.

Raman spectroscopy was performed in a Witec Alpha300RA confocal Raman-AFM spectrometer at a laser wavelength of excitation of 532 nm and 39 mW power in the range of $220–3800\ cm^{-1}$. The laser polarization angle was located in x axis. Polished glass samples around 2 mm thick were used. The precision in the determination of the Raman shifts is $\pm 1\ cm^{-1}$.

3. Results

The melting conditions for each of the final glasses obtained, chemical composition (in mol %), glass transition temperature (T_g) and content of water in ppm of H_2O have been gathered in Table 1. It can be seen that the glasses experienced several changes with the increasing temperature and melting time, such as a reduction in the content of potassium and phosphorus and, most importantly, a strong increase of the content of SiO_2, which is of 10 mol % for the LAP1 glass and reaches ca. 28% in LAP4. However, Al_2O_3 and La_2O_3 contents did not vary significantly, taking values of ca. 13% and 10%, respectively, the total loss of P_2O_5 and K_2O being compensated by the gain in SiO_2. The higher volatilization rates of potassium and phosphorus at the temperatures of melting, added to the enrichment in silica from the crucible produced such big changes in composition.

Despite the considerable loss of P_2O_5, the glass transition temperature increases only moderately from glasses LAP1 to LAP4. As it will be discussed below, the notable increase of the silica content as well as the modification of the aluminium coordination are thought to be at the origin of the increase in T_g.