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Synthesis and properties of Nd-doped oxynitride phosphate laser glasses

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ABSTRACT

The substitution of nitrogen for oxygen in phosphate glasses improves the chemical, thermal and mechanical properties and particularly reduces their very high hygroscopic character, although the preparation of homogeneous and free of defects oxynitride bulk phosphate glasses through ammonolysis represents a big challenge. This work reports on the synthesis and properties of a series of Nd-doped oxynitride phosphate glasses with composition $Na_{0.3}K_{0.3}Ba_{0.2}PO_{3-3x/2}N_x$ that may find application as laser hosts. Whereas the glass transition temperature, elastic modulus and index of refraction show a regular increase with the nitrogen content that agrees with previous studies, the effect of nitrogen onto the luminescence of Nd^{3+} ions appears to be more complicated. The average lifetime of the decay from the $^4F_{3/2}$ level decreases with the N/P ratio of the glasses, which is thought to be mainly due to the presence of water from the ammonolysis reaction. However, further thermal treatments under N_2 flow of an oxynitride glass have shown an important reduction of the water content as well as a drastic increase of the luminescence lifetime of Nd^{3+}, this being a promising method for the development of laser phosphate glasses having good chemical and mechanical properties.

1. Introduction

Phosphate glasses are known to possess large emission cross sections and low non-linear refractive indices, which are ideal for their application as solid state matrices for the emission of laser radiation. However, the use of glasses as laser hosts requires the production of generally large dimensions with a very high optical homogeneity and high quantum efficiencies, thus needing of very special processing conditions and a strict control of the glass composition. In particular, the refractive index change within the blanks must be $< 2 \times 10^{-6}$ and the absorption coefficient of the OH groups reduced to $< 5\,cm^{-1}$. Additionally, the melting of phosphate glasses may also imply certain difficulties such as those regarding high volatility of their constituents, easiness of devitrification and rapid change of the viscosity with temperature due to their higher fragile character [1]. Nevertheless, neodymium containing phosphate glasses have been successfully applied for the production of high energy laser radiation in several projects, like the National Ignition Facility (NIF) at the Lawrence Livermore Laboratory, in USA, the Gekko-XII in Osaka, Japan, and the Shenguang projects in China [2]. Currently, there is a need for developing new glasses to serve as hosts for lasers of very high average power and high repetition rate. Furthermore, the ability to choose the right composition as well as the adequate processing conditions for their preparation, lie in the precise knowledge of the atomic structure and its influence on the glass properties.

From the chemical point of view, the main constituent in laser glass compositions that provides chemical resistance and mechanical strength is aluminium [3]. Despite its advantages, alumina reduces the emission cross-section, thus being a drawback that must be taken under consideration when designing novel compositions. K_2O has been taken as the best modifier in view of its excellent characteristics to achieve large emission cross-section, long fluorescence lifetime and narrow emission band-width; however it is usual to add into the formulation other modifying oxides, such as MgO and BaO, to stabilize the glasses [4].

An alternative to have a great improvement in chemical resistance and mechanical stability of the glasses is the partial substitution of nitrogen for oxygen. This method has been studied in many glass compositions although most of them are single or mixed alkali- and alkaline-earth based glasses and is performed through a thermal treatment of the base phosphate glass under a constant NH_3 flow [5]. However, the glasses must not contain alumina in order to be able to have

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phosphate melts that keep viscosity values below 10 Pa·s at the typical temperatures of the nitridation, that range between 600 and 800 °C [6]. Unlike the nitridation in phosphate glasses, the introduction into silicate systems by ammonolysis reaction gives rise to low nitrogen contents and it usually proceeds through the melting of glass batches with nitride raw materials such as Si_3N_4, but this originates coloured, non-transparent and even partly crystallized samples [7]. Phosphate glasses are then thought to be good candidates for the development of oxynitride systems in which relatively low amounts of nitrogen introduced by ammonolysis may produce substantial changes in the chemical and mechanical properties with no need of adding Al_2O_3.

The structure of oxynitride phosphate glasses has been well studied, particularly through Nuclear Magnetic Resonance and X-ray Photoelectron spectroscopies. It is built up of PO_3N and PO_2N_2 tetrahedra that have been formed from the PO_4 groups of the oxide phosphate network [8]. On the other hand, nitrogen atoms may be bonded either to two or three phosphorus central atoms, in the form of di-coordinated (–N=) and tri-coordinated (–N <) species, respectively [9]. As a result, the bonding density and strength of the network increase significantly being at the source of the important improvement of the glass properties. So far, the majority of studies on the nitridation of phosphate glasses have concentrated on the structure and reaction mechanisms [10] and basic glass properties, whereas most recently the liquid fragility and pressure effects on their properties have concentrated the biggest efforts [11,12].

Oxynitride phosphate glasses have been mostly studied as glasses for sealing applications [13], due to their low softening temperatures and good chemical durability. Furthermore, they have also been interesting as solid state electrolytes for all-solid-state lithium batteries, due to the fact that the ionic conductivity of lithium phosphate glasses increased with the nitrogen content [14], or as bioresorbable materials thanks to the control that is possible to be exerted on their dissolution behaviour through the nitrogen content [15]. However, there is only one report on the use of Nd^{3+} doping ions as a local structural probe in nitrided $NaPO_3$ glasses [16].

In this work, we report on the preparation of transparent Nd_2O_3-doped oxynitride phosphate glasses from the system of composition Na_2O-K_2O-BaO-P_2O_5, and on their thermal, elastic and luminescence properties. We have been focused on a glass system that keeps low glass transition temperature due to the absence of alumina, while having relatively good optical performance for laser applications. The main objective was to study what are the most appropriate conditions of synthesis of oxynitride compositions aiming at developing phosphate laser glasses with low melting and transition temperatures.

2. Experimental

2.1. Synthesis

A metaphosphate base glass with composition $15Na_2O$-$15K_2O$-$20BaO$-$50P_2O_5$ (mol%) and doped with 0.5 wt% Nd_2O_3 was firstly obtained by the melt-quenching method. A batch of 100 g was prepared from reagent grade Na_2CO_3, K_2CO_3, $BaCO_3$ and $(NH_4)_2HPO_4$ and Nd_2O_3 raw materials and was calcined up to 400 °C for 24 h in a porcelain crucible, then melted at 900 °C for 2 h in air. A series of four oxynitride glasses were synthesized through ammonolysis treatment of glass pieces of the metaphosphate base glass at 650 °C under a constant flow of anhydrous NH_3 for reaction time lengths between 1 and 4 h. Three of the samples were obtained from about 10 g of the base glass (1, 2 and 4 h) while the fourth sample resulted from the nitridation of ca. 20 g of base glass. The reaction scheme is the same as the one used previously in several works and also described in details in reference [6]. It is worth noting that once the reaction with ammonia is stopped, the NH_3 is switched to pure N_2 current flow and the furnace is allowed to cool down at a free rate. Thus, the reducing atmosphere inside the furnace avoids a re-oxidation of the melt while above the glass transition temperature, and the obtained glass is annealed with no need of further treatment. The temperature was chosen to 650 °C to be the highest temperature at which no significant presence of bubbles appeared in the final oxynitride glass. Usually, higher temperatures of treatment lead to higher nitrogen contents for the same time length although the optical quality of the glasses is considerably reduced. However, it is recommended that the temperature is as high as possible because a lower viscosity of the melt facilitates the reaction with ammonia. All glass samples presented good transparency and very few of visible bubbles.

One of the oxynitride glasses having intermediate nitrogen content was submitted to further thermal treatments under pure N_2 flow at temperatures of 750 and 800 °C for 3 h. This was intended for studying the effect of melt fining on the infrared spectra, regarding the water absorption, and on the luminescence properties.

2.2. Characterisation

The composition of the phosphate base glass was analysed through X-ray Fluorescence Spectroscopy in a PANalytical MagicX 2400 spectrometer through the pearl method by mixing 0.3 g of glass with 5.5 g of $Li_2B_4O_7$. The analysed contents of the oxide components were between ± 1 mol% of the nominal ones and no contamination by SiO_2 or Al_2O_3 was found from the crucible.

The content of nitrogen in the oxynitride glasses was determined with a LECO TC-436 oxygen/nitrogen analyser using the inert gas fusion method. At least three analyses were done in the same conditions for each sample with $\sigma_{n-1} = 0.02$.

The glass transition temperature (T_g) was determined by Differential Thermal Analysis (DTA) in a SEIKO 6300 ATD/TG analyser, using platinum crucibles and a heating rate of 10 K·min^{-1} under air, and obtained at the onset of the endothermic effect shown in the DTA patterns.

Density measurements were performed by the Archimedes method using kerosene as the immersion liquid.

Optical transmittance T of the polished plates with thickness d of about 1 mm was inspected using a conventional double beam spectrometer (Hitachi, U-4100). Then, spectral dependence of absorption coefficient α was calculated using Eq. (1):

$$T \approx (1 - R)^2 \cdot \exp(-\alpha d) \quad (1)$$

where R is the reflectivity that was evaluated from transmittance (≈ 90%) in the near-infrared region.

The coefficient of absorption of hydroxyl ions was determined from the transmission Fourier-Transformed Infrared Spectra (FTIR) of the glass samples in between 450 and 5000 cm^{-1} in a Perkin-Elmer Spectrum 100 spectrometer. The coefficient of absorption of OH (α_{OH}) has been calculated from the FTIR spectra using Eq. (1) according to the method described in reference [17].

$$\alpha_{OH} = -\log(T_{3000}/T_{5000})/t \quad (2)$$

where T_{3000} and T_{5000} are the transmission at 3000 and 5000 cm^{-1}, respectively, and t the sample thickness in cm.

High Resolution Brillouin Spectroscopy (HRBS) was used to obtain information about the Young's modulus, Poisson's coefficient and refractive index of the phosphate and oxynitride phosphate glasses. The experimental setup is based on a Sandercock type 3 + 3 Tandem Fabry-Pérot spectrometer [18] and a DPSS laser (λ_0 = 532 nm) was the visible light source. Two scattering geometries (90A and Backscattering) [19] were used in order to assess the elastic and optical properties of the samples. Glass samples tested were transparent as well as elastically and optically isotropic. Fig. 1 shows graphically the meaning of the 90A and Backscattering scattering geometries. The corresponding acoustic wave vectors are: