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Highly nonlinear $Pb_2P_2O_7$-Nb_2O_5 glasses for optical fiber production

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ABSTRACT

In this study we present the production and characterization of $Pb_2P_2O_7$–Nb_2O_5 glasses and optical fibers. The dependence of Nb_2O_5 content on thermal, structural and optical properties were investigated by thermal analysis (DSC), Raman spectroscopy, UV–Visible absorption, M-Lines and Z-scan techniques. Glass transition temperature (T_g) increased linearly with Nb_2O_5 content up to 60 mol%, while thermal stability against crystallization (ΔT) reached a maximum value of 225 °C at 40 mol% of Nb_2O_5. Raman spectra showed a significant structural change by the insertion of NbO_6 octahedral units in the glass network. The increase of Nb_2O_5 concentration shifts the glasses absorption edge to lower energies, and also increases the linear refractive indexes (n_0) due to the high polarizability of niobium atoms and formation of non-bridging oxygen. Similarly to n_0, an increase in the positive values of nonlinear refractive indexes was observed using Z-Scan technique with increase of Nb_2O_5 content, based on structural changes caused by the replacement of $Pb_2P_2O_7$ instead Nb_2O_5. The average of n_2 values at 500–1500 nm raised from 2.2×10^{-19} to 3.8×10^{-19} m^2/W, when the Nb_2O_5 content was increased from 10 to 60 mol%. Lastly, a core-cladding preform was produced by suction method and the optical fiber drawn. The sample containing 40 mol% of Nb_2O_5 was used for presenting the highest thermal stability against crystallization and n_0 values > 2 from green to near-infrared wavelengths. Multimode step index fiber with good core circularity and concentricity was produced and the optical losses were determined by cut-back method at visible and near-infrared ranges.

1. Introduction

Lead pyrophosphate glasses containing tungsten oxide in the binary system $Pb_2P_2O_7$–WO_3 have already been investigated and shown interesting thermal and optical properties, resulting chemically stable, extremely high resistance against devitrification and high linear and nonlinear refractive indexes [1,2]. The optical properties were correlated with the specific phosphate glass network containing lead atoms and tungsten octahedrons. At high WO_3 contents the octahedrons WO_6 units linked together through W—O—W bonds to form highly polarizable clusters, which were pointed out to be responsible, in conjunction with lead atoms polarization, for high linear and nonlinear optical properties [2]. Besides the interesting optical properties, lead pyrophosphate glass present high vitrifying ability and unusual capability to dissolve large amounts of others glass formers, modifiers, or intermediate compounds without reduction of glass forming ability [3,4], as observed by the insertion of WO_6 inside the phosphate covalent network that form strong P—O—W bonds which are responsible to enhance the network connectivity [5].

Transparent phosphate glasses containing heavy metal oxides such as Bi_2O_3, Sb_2O_3, WO_3, Nb_2O_5, and PbO are subject of intense studies and widely exploited as optical components. In addition to the extended transparency window commonly up to 4 μm [9–13], ultrafast nonlinearity is also observed due to their nonlinear optical properties supported by the large polarizability of atoms with empty *d* orbitals (e.g. Ti^{4+}, Nb^{5+}, W^{6+}) or heavy cationic ions with an electronic configuration with ns^2 lone pair (e.g. Te^{4+}, Bi^{3+}, Sb^{3+}, Pb^{2+}) [6–9].

Poor chemical durability of most phosphate glasses is mainly due to the presence of [P—O^-] linkages, which easily adsorbs hydroxyl groups from environmental water. This feature limits their optical applications and has almost discouraged their further development as photonic devices. However, the introduction of transition metal oxide such as WO_3, Nb_2O_5, MoO_3 and TiO_2, which have several different oxidation states and high coordination number at high concentrations, gives glass formation features when combined with others glass former compound, increasing mechanical and chemical stability [14,15]. Notably, niobium phosphate glasses might be used in a varied range of applications, such as rare-earth ion hosts for laser materials, optical fibers, lenses, optical switches, electrodes and others photonics devices

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[16–18]. Teixeira et al. have studied the Na_2O–Al_2O_3–TiO_2–Nb_2O_5–P_2O_5 glass system and have demonstrated that niobium oxide is more effective than titanium oxide to improve refractive index properties and chemical durability of phosphate glass [19].

In this sense, the present work shows the study of thermal, structural and optical properties of the binary glass system $Pb_2P_2O_7$–Nb_2O_5 as a potential optical material for nonlinear applications. Linear optical properties were studied via absorption spectra and refractive index via direct and indirect optical band gap, Urbach energy and Sellmeier equation. Nonlinear optical properties were investigated by the Z-scan method to reinforce the application of these glasses as photonic materials. Further, the role of niobium oxide on glass forming ability and thermal stability was shown and the more stable composition was chosen to manufacture step-index preform and fibers by using the suction method. This method was already detailed described and used for allowing fabrication of core-cladding preform and optical fibers with good core-cladding interface and core circularity [20]. The main propose is the impact of the preform production method, e.g. the suction method, and the study of core-cladding interface and diameters for niobium lead-pyrophosphate glasses obtained as multimode optical fibers. The optical fiber was characterized regarding their structure by using optical microscopy and optical loss by cut back method, proving the photonic potential of this glass composition for optical applications, either as bulk sample and optical fiber. The possibility of fabrication of fiber with strong light confinement due to the high linear refractive indices makes niobium pyro-phosphate glasses very competitive for photonic devices.

2. Experimental

2.1. Bulk glass synthesis

The glass samples were synthesized by the conventional melt-quenching method using the raw materials Nb_2O_5 (Aldrich 99.8%) and lead orthophosphate $PbHPO_4$ prepared by precipitation of a lead salt solution with pure orthophosphate acid at room temperature, as detailed describe in [1]. Chemicals were weighted for compositions (100–x)$Pb_2P_2O_7$–xNb_2O_5 for x = 10, 20, 30, 40, 50 and 60 mol% and heated at 200 °C for 1 h to reduce adsorbed water and gases under room atmosphere, since the $PbHPO_4$ is obtained via a wet chemical route. Then, the batch was melted under open air at a temperature ranging from 950 to 1200 °C, depending on the Nb_2O_5 content for 40 min to ensure homogenization and fining. Finally, the melt was cooled inside a metal mold preheated at 20 °C below the glass transition temperature, T_g, and then annealed at these temperatures for 2 h to minimize mechanical stress resulting from thermal gradients upon cooling. For a better readability, the glasses were labeled as shown in Table 1. The bulk glass samples of very good optical quality were finally polished for optical characterizations.

2.2. Bulk glass characterization

Glass characteristic temperatures such as glass transition temperature, T_g, onset crystallization temperature, T_x, and maximum of crystallization peak, T_p, were obtained from differential scanning calorimetry in the range of 300 to 1000 °C using a NETZSCH equipment DSC 404 F3 Pegasus calorimeter, with a maximum error of ±2 °C for T_g and T_x (obtained from tangents intersection) and ±1 °C for T_p. Glass pieces of about 12 mg were set in opened platinum pans under N_2 atmosphere and a heating rate of 10 °C/min.

Absorption spectra of the glasses samples were acquired from 200 to 800 nm with a Varian Cary 5000 spectrophotometer. Raman scattering spectra were acquired at room temperature in the frequency range from 150 to 1400 cm^{-1} by using a HORIBA Jobin Yvon model LabRAM HR micro Raman apparatus equipped with a 632.8 nm laser delivering 30 mW power.

Refractive indices were measured at three wavelengths (532, 632.8 and 1550 nm) by the prism-coupler technique (M-Lines) with a Metricon-2010 instrument using a prism with refractive indices from 1.7 to 2.45 and an precision of ±0.0001. Finally, the spectra of nonlinear refractive index were obtained by refractive (closed aperture) Z-scan technique using femtosecond laser pulses.

Z-scan technique was applied to obtain the third-order optical properties, represented by nonlinear absorption and nonlinear refraction. In the refractive Z-scan method (closed aperture), the sample transmittance passing through a tiny circular aperture, placed in the far field, is monitored while the sample is translated along the z axis of a focused Gaussian beam. As the sample approaches the focus, the light intensity increased leading to the self-focus effect (for a positive nonlinear index of refraction), and therefore changing the monitored signal as a function of sample position. By fitting the experimental data according to Sheik-Bahae model [21], the nonlinear index of refraction (n_2) could be obtained according to Eq. (1):

$$T(z,\Delta\phi_0) = 1 + \frac{4\Delta\phi_0 x}{(x^2+9)(x^2+1)} \quad (1)$$

where $\Delta\phi_0$ is the one-axes phase shift defined as $\Delta\phi_0 = kn_2I_0L$, in which I_0 is the on-axis irradiance at focus, L is the sample effective thickness, $k = 2\pi/\lambda$ is the wave vector, λ is the laser wavelength, w_0 is the beam waist, and $x = z/z_0$, where z is the sample position, $z_0 = kw_0^2/2$ is the diffraction length of the beam. Removing the tiny aperture, the z-scan method enable to evaluate the nonlinear absorption (open aperture configuration) [22], represented herein by two photon absorption coefficient (β), which is determined from the experimental data through Eq. (2), assuming a temporal Gaussian pulse profile.

$$T = \frac{1}{\sqrt{\pi}q_0(z,0)}\int_{-\infty}^{\infty} \ln\left[1 + q_0(z,0)e^{-\tau^2}\right]d\tau \quad (2)$$

where, $q_0(z,t) = \beta I_0(t)L(1+z^2/z_0^2)^{-1}$. Using a dual arm setup, close and open z-scan signatures were obtained simultaneously, and the effects of two photon absorptions over nonlinear refraction have been deducted thought the ratio of both signatures.

For z-scan measurements, a Ti:sapphire chirped pulse amplified system (150-fs, 775 nm and 1 kHz) was used as the excitation source for an optical parametric amplifier, which provides 120-fs pulses from 460 up to 2000 nm, enabling to investigate the optical nonlinearities in a wide wavelength range. Depending on the excitation wavelength, the pulse energy and beam waist ranged from 4 to 200 nJ and 12 to 29 μm, respectively. The experimental error for such measurements is approximately 15%, which is based on standard deviation and measurements of fused silica as reference material. Additional information about the experimental setup can be found in the literature [8,23].

2.3. Core-cladding preform and optical fiber fabrication

The specific literature reports different techniques applied for fabrication of heavy metal oxide glasses preforms of core-cladding optical

Table 1
Molar composition of the glassy samples and their characteristic temperatures.

Sample label	$Pb_2P_2O_7$ (mol%)	Nb_2O_5 (mol%)	T_g (°C)	T_x (°C)
P9N1	90	10	427 ± 2	524
P8N2	80	20	467 ± 2	598
P7N3	70	30	526 ± 2	704
P6N4	60	40	555 ± 2	807
P5N5	50	50	568 ± 2	756
P4N6	40	60	592 ± 2	700
Core	60	40	555 ± 2	807
Cladding	57	43	559 ± 2	803