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Structural and Optical Properties of Germanoniobophosphate Glasses

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Phosphate glasses are known by their excellent chemical and mechanical properties, being used as optical fibers, biosensors, semiconductors and for many other applications due to its excellent optical transparency. Transition metal cations, such as Ti(IV) and Nb(V) are used to improve the refractive index of the glasses, beyond modifying other parameters, as molar volume, glass transition temperature and chemical durability. Similarly, Ge(IV) can also act as an intermediate cation, but in higher quantity, it is considered a glass former. Germanate glasses have a chain similar to the silicate, formed by tetrahedral GeO4 or octahedral GeO6, depending on the composition of the glass, being widely used in optical devices. It provides vibrational frequencies much lower than phosphate and silicate, with low signal loss through phonons. The objective of the present work is to evaluate the changes promoted by partial and total substitution of TiO2 by GeO2 in niobophosphate glasses chains. A series of quenched-melted niobophosphate glasses with composition 20Na2O-5Al2O3-30Nb2O5-(15-x)TiO2-xGeO2-30P2O5 , x = (0,5,10,15) mol% have been investigated with respect of its structure and optical properties with DTA, XRD, 31P MAS-NMR, mass density, chemical durability, FTIR, Raman, UV-Vis spectroscopies and refractive index. The XRD patterns confirmed the non-crystallinity of the samples. The single peak around -11 ppm of 31P MAS-NMR spectra of all the samples evidenced the main Q1 chain (pyrophosphate). There were no relevant changes in the structure of the glasses with the increase of Ge fraction until replacement of all Ti in the series. The Ti and Ge short order range could be seen with FTIR and Raman spectroscopy also, showing changes on Raman spectra profiles with appearance of a band in 930 cm-1 (attributed to LO Ge-O-Ge symmetric stretching) and decrease of octahedral TiO6 bands in 694 cm-1 and 690 cm-1, without band shift. In FTIR spectra, there were no relevant changes in the profiles of the curves, being almost the same, with a better definition of a broad band in 1200 cm-1 and 790 cm-1 due to phosphate fragments. With respect to DTA curves, the glass transition temperature, Tg, decreased from 963 K to 945 K in the series sequence. Also, the curves indicated an increase of ?T=Tx-Tg with increase the Ge ratio i.e., the chain with no Ti has a higher glass stability than the others. The mass density of the samples, measured by the Archimedes method, increased with the presence of Ge as expected, since germanium is heavier than titanium and it’s approximately an additive property. The molar volume and oxygen molar volume also increased. A better parameter with respect of the glass network is the ionic volume fraction, related with the

ionic radii of the components and the inverse of molar volume. The decreasing ionic volume radii showed that with increment of Ge quantity the main chain became less compact, so Ge acts more as a glass former than Ti, which is considered an intermediate cation. From UV-Vis spectroscopy, it was possible to evaluate the ultraviolet transmission cut-off value which exhibited a blue shift with decreasing of Ti fraction, due to charges transfer. The optical energy gap, Egap was calculated from the plot of (?E)2 as a function of E, where E is the photon energy in eV and ? the optical absorption. It resulted in an increasing of Egap value, indicating a more covalent bond of Ge-O than Ti-O, as expected. The refractive indexes were measured using a prism-coupling method at 632.8, 1305.4, and 1536.0 nm. In all wavelengths, the refractive index showed decreasing values, being non-linear. As the polarizability of dominants cations involves direct influence on the refractive index, it was expected that those values had a decrease, since Ge(IV)'s polarizability is lower than Ti(IV)'s (1.37 nm and 1.84 nm respectively). With the results of refractive index and mass density, were obtained dielectric constants, re?ection losses, molar refractivities and polarizabilities, having a decreasing rate in their values. All samples had good chemical durability, characteristic of phosphate glasses with modifiers cations. Generally, short-range order investigations suggested that the glass structure consists of Ti(IV) and Ge(IV), both in sixfold coordination and Ge fits a similar site which was Ti in the Q1 phosphate chain, becoming more covalent. With the results obtained so far, it’s proposed the preparation of ion-exchange based planar waveguides and rare-earth doped samples for potential optical amplifiers.