08-011

Heavy Metal Oxide Borate Glasses incorporated with PbF2: A comprehensive structural study by solid state NMR

Roger Gomes Fernandes, Jinjun Ren, Andrea S. S. de Camargo, Antonio Carlos Hernandes, Hellmut Eckert
Instituto de Física de São Carlos, Universidade de São Paulo (IFSC/USP) Brazil; Institute of Physical Chemistry, Westfaelisches Wilhelms Universitaet

Heavy metal oxide glasses (HMOG) have received much attention because of their high density, high linear and non-linear refractive indices enabling their use in various applications in optics and optelectronics. The use of the network former B2O3 ensures a wide glass-forming region enabling the incorporation of other constituents such as GeO2 and Bi2O3 for tailoring physical property combinations. Additionally, the incorporation of fluoride ions into these glasses is of interest because it presents a further additional opportunity for optical bandgap tuning and for using these glasses as host materials for luminescent rare-earth ions aiming at laser applications. In an effort to optimize physical properties, the glass-forming regions and local structural properties of HMOG have been extensively investigated by a great variety of spectroscopic techniques. For instance, the structural modification of borate networks by incorporated lead fluoride and other heavy metal fluoride salts is a very interesting subject from an academic point of view. In this work, a series of heavy metal oxide (HMO) glasses with composition 26.66B2O3-16GeO2-4Bi2O3-(53.33-x)PbO-xPbF2 (0 ? x ? 40) was prepared and characterized with respect to their bulk (glass transition and crystallization temperatures, densities, molar volumes) and spectroscopic properties. Homogeneous glasses are formed up to x = 30, while crystallization of ß-PbF2 takes place at higher contents. Substitution of PbO by PbF2 shifts the optical band gap towards higher energies, thereby extending the UV transmission window significantly towards higher frequencies. Raman and infrared absorption spectra can be interpreted in conjunction with published reference data. Using 11B and 19F high-resolution solid state NMR, as well as 11B/19F double resonance methodologies, we develop a quantitative structural description of this material. The fraction of four-coordinate boron is found to be moderately higher compared to that in glasses with the same PbO/B2O3 ratios, suggesting some participation of PbF2 in the network transformation process. This suggestion is confirmed by the 19F NMR spectra. While the majority of the fluoride ions is present as ionic fluoride, approximately 20% of the fluorine inventory acts as a network modifier, resulting in the formation of four-coordinate BO3/2F- units. These units can be identified by 19F{11B} rotational echo double resonance and 11B{19F} cross-polarization magic angle spinning (CPMAS) data. These results provide the first

unambiguous evidence of B-F bonding in a PbF2-modified glass system. The majority of the fluoride ions are found in a lead-dominated environment. 19F-19F homonuclear dipolar second moments measured by spin echo decay spectroscopy are quantitatively consistent with a model in which these ions are randomly distributed within the network modifier sub-domain consisting of PbO, Bi2O3 and PbF2. This model, which implies both the features of atomic scale mixing with the network former borate species and some degree of fluoride ion clustering, is consistent with all of the experimental data obtained on these glasses.