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Structure–property correlations in highly modified Sr, Mn-borate glasses

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ABSTRACT

Highly modified borate glasses with the composition $(1-2x)MnO–x(SrO–B_2O_3)$ ($x = 0.46, 0.42, 0.36, 0.25$, and 0.20) were prepared and investigated by Raman, infrared (IR), and electron paramagnetic resonance (EPR) spectroscopy. Optical properties were studied in regard to photoluminescence, optical absorption, and refractive index. The Mn^{2+}/Mn^{3+} equilibrium was shifted towards the divalent manganese ion as a result of the strongly reducing melting conditions employed in this work, which facilitate the preparation of transparent glasses with up to 80 mol% total SrO and MnO content. Changes in the optical and physical properties within this glass series were related to structural variations. The structure of glasses with relatively low MnO content was found to involve mainly trigonal $[BØ_2O]^-$ and tetrahedral $[BØ_4]^-$ metaborate groups, which are replaced progressively by pyroborate $[B_2O_5]^{4-}$ and orthoborate $[BO_3]^{3-}$ triangular units upon increasing MnO content. At the highest modification level ($x = 0.20$) the structure is built of orthoborate isomeric species in triangular $[BO_3]^{3-}$ and tetrahedral $[BØ_2O_2]^{3-}$ configuration. The latter species form $[B_3O_9]^{9-}$ rings, which reestablish some degree of network connectivity, as they involve three bridging and six non-bridging oxygen atoms, and this is reflected by the increase of the glass transition temperature for $x = 0.25$ over $x = 0.20$. Micro-Raman measurements showed structural inhomogeneities in these glasses due to chemical isomerization processes involving short- and medium-range order structures. Also, increasing MnO content was shown to cause MnO-clustering in the glasses as revealed by luminescence and EPR measurements.

1. Introduction

Borate glasses have been studied extensively regarding the effect of glass composition on structural properties [1–10]. Much attention was focused on the boric oxide anomaly, as trigonal uncharged $[BØ_3]$ entities transform upon the addition of modifier oxide initially into $[BØ_4]^-$ tetrahedra and only as the modifier oxide concentration increases further non-bridging oxygen atoms are formed on $[BØ_2O]^-$ and $[BØO_2]^{2-}$ entities, until finally $[BO_3]^{3-}$ monomers are generated (Ø = bridging and O = non-bridging oxygen atom, see also Schematic 1). This unique behavior of borate glasses is, for example, utilized in low alkaline borosilicate glasses as the incorporation of $[BØ_4]^-$ tetrahedra improves considerably the handling of silica glass without significantly degrading its properties, such as refractive index or photo induced nonlinear effects [11,12].

High amounts of network modifying oxides can be incorporated into borate glasses, including rare earth, transition-metal, or post-transition metal oxides. This capacity of borate glasses makes them interesting matrix materials for various applications ranging from waste immobilization [13,14] or low temperature sealing glasses [15] to promising new uses in the field of non-linear optics or fiber optics [16], since high concentrations of easily polarizable heavy metal cations lead to very high refractive indices and high susceptibilities.

Transition metal ions can act either as network formers or modifiers depending on their redox state and coordination number [17]. Network forming properties are often associated with tetrahedral coordination and network modification with octahedral bonding configuration of the cation. Transition metal ions such as manganese also influence the mechanical, optical, magnetic and electrical properties of glasses [18–21] and consequently a wide range of spectroscopic methods are used in the study of such glasses. Information on the ion valence, site geometry, or bonding characteristics can thus be deduced. Methods such as fluorescence and EPR spectroscopy are very selective and in the case of manganese are only sensitive for divalent Mn^{2+} [9,10,19,20,22–24]. Other methods such as UV–Vis spectroscopy provide information on all oxidation states, i.e. in the glasses of this study on Mn^{2+} and Mn^{3+} [9,10,19,20,22,25–27].

Binary $SrO–B_2O_3$ glasses with concentration close to 50 mol% SrO were successfully melted by various groups [28,29]. By rapid quenching methods the modifier oxide content in $Li_2O–B_2O_3$ or $PbO–B_2O_3$ glasses could be raised to as high as 75 mol% [8,30]. The $MnO–B_2O_3$ system is hitherto studied less thoroughly. One study on the incorporation of manganese in low alkaline borosilicate glasses was restricted to relatively low MnO levels of up to 4 mol%, at

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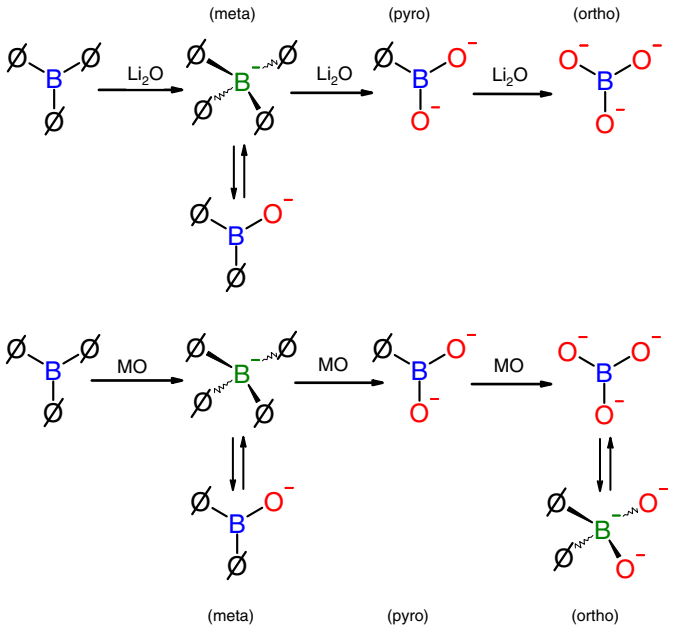

Schematic 1. Structural evolution in borate glass series: $Li_2O–B_2O_3$ (top) and $MO–B_2O_3$ (bottom). Only short-range order units are included for reasons of simplicity.

which point phase separation started to set in [10]. A binary, fully reduced Mn(II)O–B_2O_3 metaborate glass was obtained by Ehrt et al. [9,10] after liquid–liquid phase separation of the melt, as a borate rich phase protected the heavier binary MnO–B_2O_3 melt from the oxidizing influence of the atmosphere. However, a conventionally melted 50MnO–50B_2O_3 (mol%) glass is deep black, due to the high fraction of Mn^{3+} [9,10]. Stabilizing divalent manganese ions in binary and ternary glass systems of high modifier content is challenging as such glasses, with their high optical basicity, also tend to favor the higher oxidation states of polyvalent additives. Therefore strongly reducing conditions were applied in this work to prepare borate glasses in the series $(1-2x)$MnO–x(SrO–B_2O_3) (MSB glasses). Various spectroscopic techniques were applied to study the structure of these glasses, including the interconnectivity of Mn(II)O_x polyhedra with different borate entities and its influence on thermal, physical, optical, magnetic and structural properties.

2. Experimental

2.1. Sample preparation

Glasses with the nominal composition $(1-2x)$MnO − x(SrO–B_2O_3) with x = 0.46, 0.42, 0.36, 0.25, and 0.20 were melted in an inductively-heated furnace at 1300 °C for 30 min using SiC-C crucibles. The release of C and CO from the crucible ensures strongly reducing conditions during melting. The batch of raw materials (Mn_2O_3, SrO and H_3BO_3 of high purity) was placed into the furnace at 700 °C and then heated up to 1300 °C with a heating rate of approximately 20 K/min. To prevent devitrification, the melts had to be quenched between steel plates. Using this method, it was possible to obtain stable glasses without crystallization for B_2O_3 contents as low as 20 mol%. The glass with x = 0.50 (i.e. strontium–metaborate, SrO–B_2O_3) could not be prepared, as the glass-forming region in the binary strontium-borate system extends only up to 47 mol% SrO [29]. Therefore, the binary glass 0.47SrO–0.53B_2O_3 was prepared and its Raman and IR spectra were measured for the purpose of comparison with the MnO-containing SrO–B_2O_3 glasses. The amorphous state of the samples was verified by XRD measurements which showed no signs of crystallinity in any of the samples.

2.2. Sample characterization

The density was measured by the Archimedes method using distilled water with a drop of detergent as immersion liquid. Differential scanning calorimetry (DSC) data were collected from 20 °C to 1200 °C with a heating rate of 20 K/min in N_2 atmosphere. Refractive indices were measured with an Abbé refractometer at 589 nm (Na: D-line). The tail of the Mn-absorption band extends to 589 nm where the refractive index was measured and, thus, prevents refractive index measurement of the sample with the highest MnO concentration. The optical basicity was calculated after the increment method as described by J. Duffy [27,31] and also from the position of the optical absorption bands of Mn^{2+} [19,20,26,27]. More details will be provided in Section 3.2.2, where also the calculated oxygen polarizability is described.

2.3. Spectroscopy

All spectroscopic analyses were performed at room temperature and if not otherwise mentioned polished plane-parallel sample plates, with a thickness of 0.75 to 1.5 mm, were used in the acquisition of the spectral data. Raman spectra were obtained with a dispersive confocal Raman microscope in the range from 100 to 1600 cm^{-1} with a resolution of 2 cm^{-1} using the 488 nm laser excitation line. Infrared (IR) measurements were carried out on polished glass samples using a vacuum IR spectrometer. The spectra were taken in reflectance mode with an incidence angle of ~11°, in the range of 30–7000 cm^{-1} with a resolution of 2 cm^{-1}. A total of 200 scans were collected and the average of the scans is used for evaluation. The spectra were analyzed by Kramers–Krönig transformation as detailed in Reference [6] to yield the absorption coefficient spectra, $\alpha(\nu)$, from the expression $\alpha(\nu) = 4\pi\nu k(\nu)$ where $k(\nu)$ is the imaginary part of the complex refractive index and ν is the infrared frequency in inverse centimeters.

UV–Vis measurements were obtained in the transmission mode in the range from 200–1200 nm. The spectra were converted into absorbance and normalized to the sample thickness (optical density in cm^{-1}). Commercial software was used for the Gaussian deconvolution. Photoluminescence spectra were obtained from all samples with a high-resolution spectrofluorometer equipped with excitation and emission double monochromators. A static Xe lamp (450 W) and a Xe flashlamp (75 W) were used as excitation sources for the static and dynamic measurements respectively. Both lamps work in the visible and the slit width in both, the excitation and the emission monochromators, was set at 3 nm for all measurements. EPR measurements were obtained for structural and magnetic investigations. The experiments were conducted on an instrument, which provided internal g- and spin calibration. In order to compare samples with so different MnO concentrations, powdered samples of the same weight were diluted by EPR inactive SiO_2 powder and standardized sample tubes were filled to exactly the same level. The shown spectra were further normalized to the same EPR intensity for better comparison.

3. Results and discussion

3.1. Physical properties

The measured physical properties including glass transition temperature T_g, density, refractive index, and optical basicity are listed in Table 1 and are shown as a function of composition in Fig. 1. Different trends for the different properties are apparent within the glass series. The glass transition temperature T_g decreases with increasing total metal oxide content (Fig. 1a), except for the x = 0.20 sample which has the highest level of modification (i.e., with only 20 mol% B_2O_3). We note that T_g data for alkali-borate and alkaline-earth borate glasses were reported over extended ranges of composition by Feller