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Supplementary Information

Short-range structure, the role of bismuth and property-structure correlations in bismuth borate glasses

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S1. Application of infrared spectroscopy for the calculation of the molar fractions of the borate species present in glasses x=0.50 and 0.60 of the system xBi_2O_3-(1-x)B_2O_3.

Based on the discussion in Sections 3.1 and 4.1, the borate speciation in glasses x=0.50 and 0.60 involves pyro-borate $BØO_2^{2-}$ and ortho-borate BO_3^{3-} trigonal units and tetrahedral units in the form of either meta-borate $BØ_4^-$ or ortho-borate $BØ_2O_2^{3-}$ species. For the evaluation of the corresponding molar fractions we consider the mass balance equation:

$$X_{4m} + X_{4o} + X_1 + X_0 = 1 \quad \text{(S.1)}$$

X_{4m}, X_{4o} denote the molar fraction of the $BØ_4^-$ and $BØ_2O_2^{3-}$ tetrahedral units, and X_1, X_0 are the molar fractions of $BØO_2^{2-}$ and BO_3^{3-} triangular units, respectively. Besides Eq. (S1), we apply a pair of equations similar to Eqs. (15) in the manuscript for the two component bands in Table 2 with frequency ν_2 and ν_3 in the ranges 1290-1315 cm^{-1} and 1185-1199 cm^{-1}, respectively:

$$A_2 = (X_1 + X_0)\, a_{B-O^-} \qquad \text{(S.2a)}$$

$$A_3 = X_1\, a_{B-Ø} + 0.14\, X_0\, a_{B-O^-} \qquad \text{(S.2b)}$$

where A_2 and A_3 are the normalized integrated intensities of the bands with frequency ν_2 and ν_3, respectively. Using the previously calculated values for $a_{B-O^-} = 0.785\ cm^{-2}$ and $a_{B-Ø} = 0.4624\ cm^{-2}$, the molar fractions of pyroborate species $BØO_2^{2-}$, X_1, and orthoborate species BO_3^{3-}, X_0, can be evaluated directly from Eqs. (S.2a) and (S.2b) as follows:

$$X_0 = \frac{A_3 - A_2 \dfrac{a_{B-Ø}}{a_{B-O^-}}}{(0.14\, a_{B-O^-}) - a_{B-Ø}} \qquad \text{(S.3)}$$

$$X_1 = \frac{A_2}{a_{B-O^-}} - \frac{A_3 - A_2 \dfrac{a_{B-Ø}}{a_{B-O^-}}}{(0.14\, a_{B-O^-}) - a_{B-Ø}} = \frac{A_3 - 0.14 A_2}{a_{B-Ø} - 0.14\, a_{B-O^-}} \qquad \text{(S.4)}$$

The calculated molar fractions through Eqs. (S.1), (S.3) and (S.4) for the glass x=0.50 are $X_1 = 0.145$, $X_0 = 0.447$ and $X_4 = X_{4m} + X_{4o} = 0.408$, whereas for the glass x=0.60 the corresponding values are $X_1 = 0.089$, $X_0 = 0.576$ and $X_4 = X_{4m} + X_{4o} = 0.335$. The individual fractions X_{4m} and X_{4o}were obtained by employing Eqs. (19) of the manuscript, resulting in $X_{4m} = 0.366$ and X_{4o}=0.042 for x=0.50 and $X_{4m} = 0.281$ and X_{4o}=0.054 for x=0.60. The obtained relative fractions X_{4m}/X_4 are and X_{4o}/X_4 are shown in Fig. 8b.