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Optical properties of bismuth borate glasses

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Abstract

Optical properties of glasses in the binary system bismuth oxide (Bi_2O_3)–boric oxide (B_2O_3) are measured for the composition range 25–65 mol% Bi_2O_3. Both, refractive indices and ultraviolet absorption edge, show an expressed dependence on composition. A generalized Sellmeier formula is derived to describe the refractive indices for the whole composition range and a wide wavelength range.

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1. Introduction

Boric oxide, B_2O_3, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B_2O_3 exhibit rather high viscosity and tend to the formation of glasses. In crystalline form, on the other hand, borates with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties (for a recent review read e.g. Ref. [1]). The boron atom usually coordinates with either three or four oxygen atoms forming $[BO_3]^{3-}$ or $[BO_4]^{5-}$ structural units. Furthermore, these two fundamental units can be arbitrarily combined to form different B_xO_y structural groups [2]. Among these borates, especially the monoclinic bismuth borate BiB_3O_6 shows up remarkably large linear and nonlinear optical coefficients [3,4]. Calculations indicate that this can be mainly attributed to the contribution of the $[BiO_4]^{5-}$ anionic group [5,6]. For the linear properties (refractive index) this anionic group should act in a similar way in an amorphous environment, i.e., in glass. Combining bismuth oxide with boric oxide thus allows to tune the optical properties in a wide range depending on the composition. Consequently, the properties of glasses of the system Bi_2O_3–B_2O_3 have attracted much interest [7]. The present work intends to give a description of the optical properties of this glass system over a wide composition range. Refractive indices and absorption are measured and described numerically by appropriate fits.

2. Experimental

Samples of bismuth borate glasses $(Bi_2O_3)_x(B_2O_3)_{1-x}$ with compositions spanning the range $x = 0.25 \ldots 0.65$ were fabricated from melts of corresponding compositions. The melts were thoroughly homogenized at a temperature of ≈1000 K and then cooled down to room temperature at a rate of 100 K per hour.

For the absorption measurements, a Bruins Omega 10 spectrometer was used working in the near ultraviolet, visible, and near infrared spectral region. The absorption data were measured on plate-shaped samples with a thickness of approximately 1 mm. The data were corrected for reflection using our measured refractive index values.

The measurements of the refractive indices were carried out on a high resolution goniometer using the prism method on thoroughly fabricated prism-shaped samples. From the minimum deflection angles φ for discrete spectral lines of several light sources the refractive indices are calculated according to

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$$n = n_{\mathrm{air}} \frac{\sin(\gamma/2 + \varphi/2)}{\sin(\gamma/2)}. \quad (1)$$

In Eq. (1), γ denotes the prism angle which was between 30° and 35° for our samples.

The refractive index of air n_{air} is calculated using Edlén's [8] approximation (wavelength λ in μm)

$$n_{\mathrm{air}} = 1 + 10^{-4}\left[0.834213 + \frac{240.603}{130 - \lambda^{-2}} + \frac{1.5997}{38.9 - \lambda^{-2}}\right]. \quad (2)$$

3. Results and discussion

To investigate the contribution of the $[BiO_4]^{5-}$ anionic group on the linear optical properties of bismuth borate glasses we compared the refractive indices of crystalline bismuth borate BiB_3O_6 with those of glass with identical composition ($x = 0.25$). The comparison is shown in Fig. 1.

Refractive index data for the crystalline BiB_3O_6 are taken from Ref. [4]; a comparison to calculated index data [6], unfortunately, is not possible, as these authors based their calculations on the crystal coordinate system instead of the optical one.

Our measured values can be well described by a modified Sellmeier dispersion relation (wavelength λ in μm)

$$n^2(\lambda) = A + \frac{B}{\lambda^2 - C} - D\lambda^2, \quad (3)$$

where $A = 3.2141$, $B = 0.0456$, $C = 0.0349$, $D = 0.0235$.

The comparison between crystal and glass shows that the (averaged) refractive indices in the blue spectral region are practically identical whereas in the red and infrared region the indices in the glass are lower. This strongly indicates that also in the glass $[BiO_4]^{5-}$ anionic groups are present and are contributing to the electronic portion to the refractive index. In the red and infrared where the phonon contribution is important the refractive index of the glass becomes lower than that of the crystal. This is due to the more disintegrated amorphous structure which reduces the phononic portion.

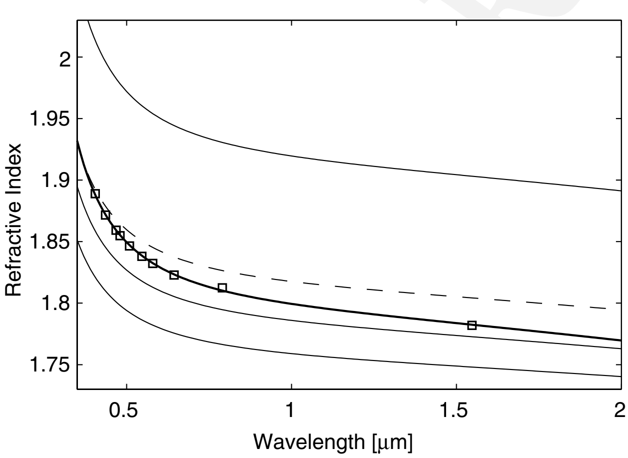

Fig. 1. Comparison of the refractive indices of crystalline bismuth borate BiB_3O_6 with those of bismuth borate glass of the same composition. Thin full lines represent the three refractive indices of crystalline BiB_3O_6 [4], the dashed line is the average of the three crystal indices. Squares indicate measured data of the glass, the thick line is a Sellmeier approximation to the data.

The conformance for the composition $x = 0.25$ indicates that also for other compositions the existence of $[BiO_4]^{5-}$ anionic groups in the glasses and their contribution to the refractive index may be treated in a similar way. To prove this, we measured the refractive indices for glasses of several compositions between $x = 0.25$ and 0.65 and fitted the measured values with a generalized Sellmeier dispersion relation. As an ansatz for this modified Sellmeier relation for the refractive index n as a function of wavelength λ (in μm) and composition x (bismuth oxide content) we propose

$$n^2(\lambda, x) = A_0 + A_1 \cdot x + A_2 \cdot x^2 + \frac{B_1 \cdot x}{\lambda^2 - C_0 - C_1 \cdot x} - D_0 \cdot \lambda^2. \quad (4)$$

A nonlinear least squares fit to the measured values yields the coefficients summarized in Table 1. The mean squared error of the fit is $\langle\sigma^2\rangle = 2.9 \times 10^{-6}$.

The Sellmeier ansatz of Eq. (4) implicates the assumption that for the short wavelength region mainly the bismuth oxide group is responsible, i.e., the influence of the UV oscillator is assumed to be strictly proportional to the Bi_2O_3 content ($B_0 = 0$ omitted and $B_1 \neq 0$ included in the ansatz). This was verified by allowing for B_0 as an additional fit parameter which yielded a very small value for B_0 and no noticeable improvement of the fit.

Several fit curves together with the respective measures values are shown in Fig. 2. The excellent agreement shows that the proposed Sellmeier relation can be applied in a concentration range spanning $x = 0.2 \ldots 0.7$ and in a wavelength range $\lambda = 0.4 \ldots 1.6$ μm with an accuracy of at least 10^{-3}.

A similar strongly expressed dependence on the Bi_2O_3 content is found for the position of the short wavelength

Table 1
Coefficients for the generalized Sellmeier dispersion relation given in Eq. (4)

Coefficient	Value
A_0	1.90598
A_1	5.78900
A_2	−2.22010
B_1	0.16995
C_0	0.02116
C_1	0.09230
D_0	0.01857

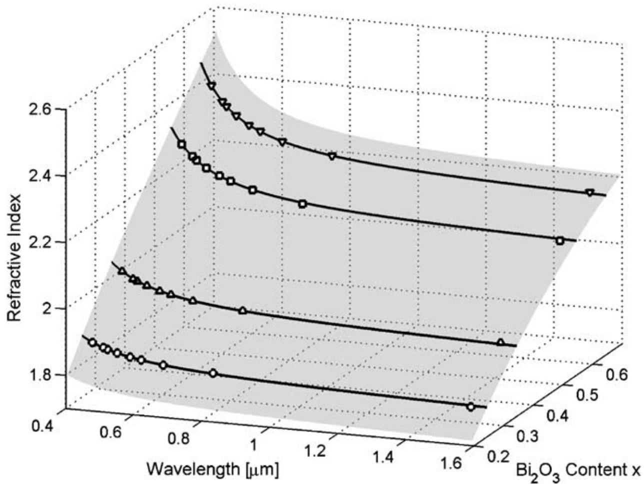

Fig. 2. Refractive indices of bismuth borate glasses. Sketched are measured values (···) and fit curves (—) for Bi_2O_3 contents of 0.25, 0.35, 0.55, and 0.65. The surface defined by the generalized Sellmeier relation (Eq. (4)) is shaded in gray.

absorption edge of the glasses. The measured absorption curves for the visible, ultraviolet, and near infrared region are summarized in Fig. 3. All data are corrected for reflection using the refractive index data.

The short wavelength absorption edge shifts to longer wavelengths with increasing Bi_2O_3 content. As shown in the inset, this shift can be approximated by a linear relation. For an absorption coefficient of $\alpha = 10$, a linear fit yields

$$\lambda_{\alpha=10} = 0.316 + 0.187 \cdot x \quad (\lambda \text{ in } \mu\text{m}). \tag{5}$$

This can be compared with the position of the ultraviolet oscillator defined in the Sellmeier relation (Eq. (4))

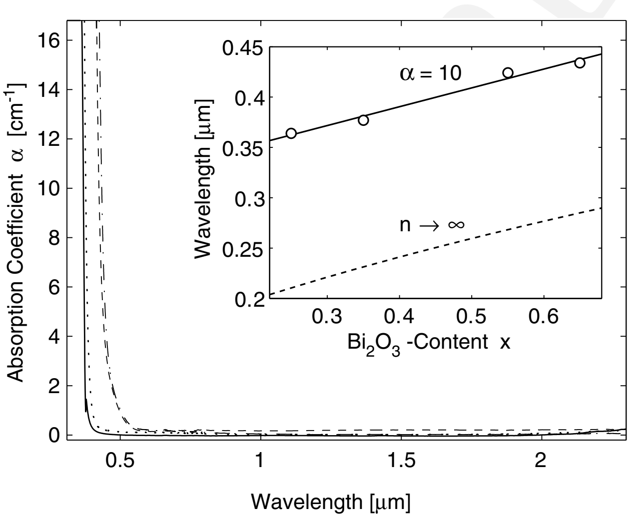

Fig. 3. Optical absorption of bismuth borate glasses with Bi_2O_3 contents of 0.25, 0.35, 0.55, and 0.65 (left to right). The inset shows the position of the short wavelength absorption edge ($\alpha = 10$) as a function of the Bi_2O_3 content (dots and full line). The dashed line shows the wavelength position of the ultraviolet oscillator as defined by the generalized Sellmeier relation (Eq. (4)).

$$\lambda_{0,\mathrm{UV}} = (C_0 + C_1 \cdot x)^{1/2}, \tag{6}$$

which is plotted as dashed line in the inset ('$n \to \infty$'). The two dependencies, short wavelength absorption edge and position of the ultraviolet oscillator in the Sellmeier fit show exact correspondence, a linear fit to the oscillator wavelength yields

$$\lambda_{0,\mathrm{UV}} = 0.165 + 0.186 \cdot x \quad (\lambda \text{ in } \mu\text{m}), \tag{7}$$

i.e., the identical slope as in Eq. (5). This again is a strong indication that the optical properties of bismuth borate glasses in the short wavelength region are predominantly governed by the bismuth oxide groups.

4. Conclusion

It could be shown that the optical properties of bismuth borate glasses are mainly influenced by the bismuth oxide group, at least in the short wavelength region. A generalized Sellmeier relation allows to describe the refractive index of the glasses in a wide composition and wavelength range. The fit to the measured values reveals that the oscillator strength of the ultraviolet oscillator in the Sellmeier relation is strictly proportional to the bismuth oxide content. A similar approximately linear dependence is found for the short wavelength absorption edge and for the wavelength position of the ultraviolet oscillator.

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