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LOW-MELTING BISMUTH–BORATE GLASS: COMPOSITION DEVELOPMENT

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The properties of low-melting lead-free glass based on the system $ZnO–Bi_2O_3–B_2O_3$ with K_2O, Al_2O_3, and SiO_2 additions are studied experimentally and the results are presented. The complete spreading and softening temperature ranges are determined. The computed values of the CLTE and refractive indices of the glasses are presented. Conclusions are drawn concerning the structural state of the bismuth ions.

Key words: low-melting glass, bismuth-borate system, complete spreading temperature, linear thermal expansion coefficient, refractive index, structural state of bismuth ions.

Highly economical sources of high-intensity general lighting based on LEDs (Light Emitting Diodes) are being actively developed [1]. Such devices require the development of converters-diffusers consisting of a glass bulb or plate whose inner surface is coated with a glaze coating consisting of a low-melting, alkali-free, low-lead or lead-free glass with CLTE close to that of the glass substrate and a nanosize filler — a luminophor evenly distributed within the interior volume of the coating. The most commonly used luminophor is CeO_2-doped crystalline yttrium-aluminum garnet $3Y_2O_3 \cdot 5Al_2O_3$ (YAG). The role of the luminophor is to convert the blue light of the LED into white light. Barium crown glass or flint glass can be used for the substrate glass [2]. However, ordinary sheet glass with the LED positioned away from it is also admissible as a substrate.

The requirements for glass as a base for a composite glass coating can be formulated as follows:

1) the CLTE must be comparable to that of the glass substrate ($(75 – 90) \times 10^{-7}\ K^{-1}$);

2) the complete spreading temperature during heat treatment must not exceed 650 – 700°C;

3) the softening temperature must be 450 – 530°C;

4) the refractive index must be at least 1.6, but even better 1.7 (taking account of the high refractive index of the YAG fill);

5) the chemical stability must no lower than third class.

On the basis of these requirements, i.e., to secure a very low complete spreading temperature and high CLTE and refractive index, bismuth-borate glasses are of greatest interest. A prerequisite for synthesizing low-melting glass in such systems with such a low spreading temperature is the presence of low-melting compounds and eutectics in the system $Bi_2O_3–B_2O_3$ [3]. Five chemical compounds with the following compositions form in this system: 1) $12Bi_2O_3 \cdot B_2O_3$; 2) $2Bi_2O_3 \cdot B_2O_3$; 3) $3Bi_2O_3 \cdot 5B_2O_3$; 4) $Bi_2O_3 \cdot 3B_2O_3$; and, 5) $Bi_2O_3 \cdot 4B_2O_3$. The melting temperatures of these substances are, respectively, as follows: 632 (incongruent melting), 675, 722, 708, and 715°C (congruent melting). In addition, four eutectics with the melting temperatures 622, 646, 698, and 696°C are present in the same system. Thus, glass based on this system can be expected to have quite good flowability at the coating deposition temperatures, i.e., below 700°C.

To secure higher chemical stability, the ternary system $ZnO–Bi_2O_3–B_2O_3$ was chosen as the base for the present investigations. Low glass-melting temperature in this system is also guaranteed by the formation of low-melting eutectics in the systems $ZnO–B_2O_3$ (961°C) and $ZnO–Bi_2O_3$ (750°C) [3].

It has been shown that in the system $ZnO–Bi_2O_3–B_2O_3$ glass forms in a wide range of temperatures (Fig. 1) [4]. However, even though there is heightened interest in this system as a base for synthesizing glass-solders and glass for optical devices there are practically no systematic data on the properties of glasses belonging to it. Some data on the optical and physical properties of $ZnO–Bi_2O_3–B_2O_3$ glass are presented in [5]. Glass with the following compositions was

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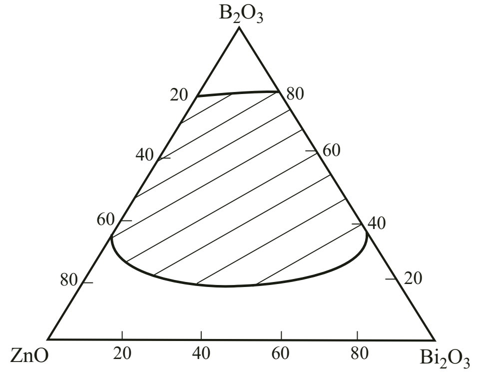

Fig. 1. Glass formation region in the system $ZnO–Bi_2O_3–B_2O_3$ [4].

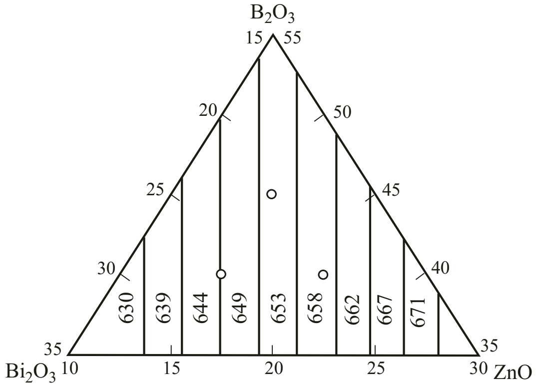

Fig. 2. The temperature $t_{z.m}$ (the numbers inside the triangle correspond to $t_{z.m}$, °C) versus the composition with constant content $SiO_2 + Al_2O_3 + K_2O = 20$ wt.%.

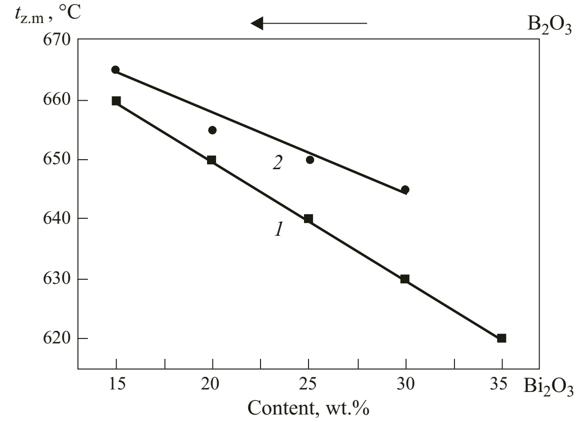

Fig. 3. Effect of the substitution of Bi_2O_3 for B_2O_3 on $t_{z.m}$ with ZnO content 10 wt.% (*1*) and 15 wt.% (*2*).

studied (molar content, %): 15 – 70 Bi_2O_3; 15 – 40 ZnO; and, 15 B_2O_3. The glass density with Bi_2O_3 content increasing from 45 to 70% varies in the range 5.91 – 6.32 g/cm^3, the molar volume is 42.71 – 55.13 cm^3/mole, and the vitrification temperature t_g is 501 – 492°C. The IR-spectroscopy data for such glass show absorption bands at 420 – 450 and 480 cm^{-1} due to the Bi–O bonds in the $[BiO_3]$ and $[BiO_6]$ groups [5]. As the Bi_2O_3 content decreases the latter absorption band shifts from 480 to 523 cm^{-1} because of the lower local symmetry in the $[BiO_6]$ polyhedra. Data on the properties of low-melting solder glasses in the quaternary system $ZnO–Bi_2O_3–B_2O_3–SiO_2$ with molar contents SiO_2 20, 30% and B_2O_3 10, 20, 30% are presented in [6]. It has been established that the vitrification temperature changed from 411 to 522°C, the dilatometric softening temperature T_d from 453 to 563°C, and the CLTE from 53×10^{-7} to 95×10^{-7} K^{-1}.

On the basis of the published data glass compositions having the properties required to obtain glass-composite coatings were developed in the system $ZnO–Bi_2O_3–B_2O_3$ with SiO_2 and Al_2O_3 introduced into all glasses to stabilize the glassy state and K_2O to activate the transition of triply into quadruply coordinated boron (total mass content $SiO_2 + Al_2O_3 + K_2O = 20\%$). The content of the main components by weight was varied within the following limits (%): 10 – 30 ZnO, 15 – 35 Bi_2O_3, and 35 – 55 B_2O_3. The glass compositions were varied in accordance with a quartic Scheffé plan with variation step 5% (content by weight). The raw materials were zinc and bismuth oxides, boric acid, quartz sand, and potassium nitrate.

The glass was made in corundum crucibles at temperatures 1000 – 1100°C with soaking time 1 h and annealed at temperature 400°C. Under these conditions all glasses were completely founded and fined. To determine the crystallizability and the complete spreading temperatures (zero meniscus temperature $t_{z.m}$) the glasses were heat-treated in a gradient furnace in the temperature interval 450 – 900°C for 1 h. The experimental glasses different with respect to stability of the glassy state and do not show any indications of crystallization.

The following properties were studied for all glasses: crystallizability, complete spreading temperature $t_{z.m}$ — the zero-meniscus temperature on the gradient crystallization boat, softening temperature, CLTE, and chemical stability (water resistance). In addition, values of the CLTE and refractive index were computed.

The complete spreading temperature in the system versus the composition is shown in Figs. 2 and 3. It is clearly seen that bismuth oxide has the greatest effect on $t_{z.m}$ as its content increases at the expense of both B_2O_3 and ZnO, i.e., with increasing ratios Bi_2O_3/B_2O_3 and Bi_2O_3/ZnO. The complete spreading temperatures $t_{z.m}$ of the glasses in the system vary from 610 to 655°C and are determined by, first and foremost, the Bi_2O_3 content.

The softening temperature of the experimental glasses lies in the range 450 – 550°C while $t_{z.m}$ versus the composition agrees almost completely with the variation of the complete spreading temperature. That is to say, glasses with the highest Bi_2O_3 content characteristically have the lowest values of $t_{z.m}$ while glasses with the highest zinc content have the highest values.

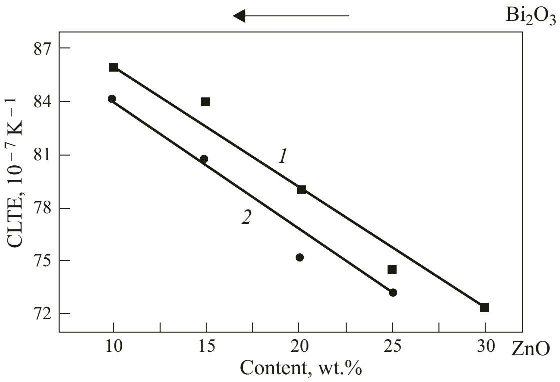

Fig. 4. Effect of replacing Bi$_2$O$_3$ with ZnO on the CLTE with B$_2$O$_3$ content 35 wt.% (*1*) and 30 wt.% (*2*).

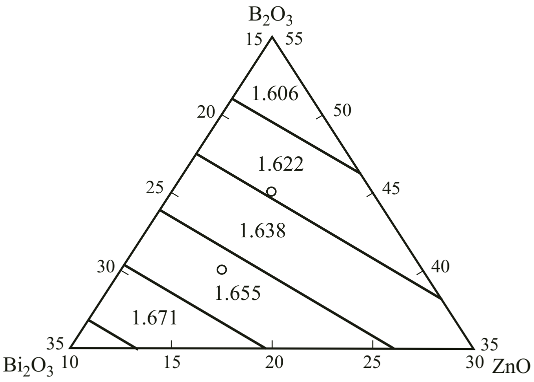

Fig. 5. Refractive index versus the composition of glasses with constant content SiO$_2$ + Al$_2$O$_3$ + K$_2$O = 20 wt.%.

The experimental values of the CLTE were in the range $(72 - 86) \times 10^{-7}$ K^{-1}. It is interesting to compare the experimentally measured and computed values of the CLTE. The data required to calculate the CLTE in borate systems were taken from [7], according to which in borate glasses the partial additive value 55×10^{-7} is proposed for B$_2$O$_3$ and 130×10^{-7} for Bi$_2$O$_3$. A. A. Appen's partial additive values are used for all other components [8]. The computed values of the CLTE are $(78 - 87) \times 10^{-7}$ K^{-1} (see Table 1). Using the partial numbers proposed in [7] and comparing them with the experimental values gave a discrepancy in the range $(0.5 - 4.0) \times 10^{-7}$ K^{-1} in the direction of higher values. This data confirm the validity of using for borate glasses the partial numbers proposed in [7] for B$_2$O$_3$ and Bi$_2$O$_3$. A plot of the CLTE versus the ratio Bi$_2$O$_3$/ZnO in the experimental system is displayed in Fig. 4. The large increase of the CLTE with increasing Bi$_2$O$_3$ content is due to the fact that the bismuth ion has the largest ionic radius (0.12 nm) of all cations in the system.

Figure 5 displays the computed refractive indices n_D of the experimental glasses. It was found that the effect of Bi$_2$O$_3$ on n_D is comparable to that of ZnO, though even here Bi$_2$O$_3$ predominates.

Thus, practically all of the experimental glasses meet the necessary requirements with respect to a set of properties.

Glasses with Bi$_2$O$_3$ content 15, 20, and 25 wt.%, which were used as a base to prepare powder mixtures with 10 and 15% fine-crystalline YAG added, were chosen to obtain the experimental light-converting composite-glass coatings. After being carefully ground in a porcelain mortar the powder was mixed with isopropyl alcohol, deposited on glass plates, dried at temperature 50°C, and kilned at 650°C. The experimental glasses were used as a base to obtain coatings of satisfactory quality with well-evidenced light-conversion properties.

The role of Bi$_2$O$_3$ in glass-forming melts and the structural and coordination state of bismuth ions in glasses are of special interest. Research on bismuth-containing glasses from the standpoint of the structural state of bismuth ions has been stepped up recently. Studies of glasses in the system BaO–Bi$_2$O$_3$–B$_2$O$_3$ have led to the conclusion that the principal coordination state of bismuth ions in the systems is octahedral with [BiO$_6$] groups being formed while the bismuth ions are in the charge state Bi^{3+} [9]. In our opinion it can be concluded on the basis of the ionic radius of the bismuth ion — 0.12 nm and the ratio $r_{\mathrm{Bi}^{3+}}/r_{\mathrm{O}^{2-}} = 0.88$ that a coordination number for bismuth ions with respect to oxygen of less than 6 is not substantiated theoretically, and the supposition that the structural groups [B iO$_3$] are formed is very problematic. IR-Spectroscopic studies of bismuth–oxygen compounds have established that the vibrations of Bi–O bonds make the largest contribution to the IR spectra in the region $150 - 500$ cm^{-1}, which also confirms the quite high coordination number of bismuth ions in bismuth-oxygen polyhedra. These are the vibrations of Bi–O bonds to which the absorption bands $420 - 430$ and $470 - 490$ cm^{-1} in the IR spectra are associated in [5, 7].

A study of Bi$_2$O$_3$–B$_2$O$_3$ glasses has also noted that bismuth in the form of the structural groups [BiO$_6$] and not [BiO$_3$] is present in glass [11].

TABLE 1. Experimentally Measured and Computed CLTE Values for Glasses

Index	CLTE, 10^{-7} K^{-1}, for glasses														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Computed values	79.0	79.6	82.8	84.1	85.9	74.7	75.9	80.7	84.0	74.0	75.2	79.0	73.2	74.5	72.4
Experimental values	78.5	80.4	82.6	85.0	87.7	78.5	80.4	82.6	85.1	78.4	80.4	82.6	78.3	80.4	78.3

In addition, the high maximum values of the molar content of bismuth oxide which can be introduced into glass (> 80%) draw our attention [10]. The likelihood of obtaining a transparent optical glass with Bi_2O_3 content to 90 wt.%, containing TeO_2 or SeO_2 as well as RO and R_2O components, where RO is Zn, Ba, Sr, Ca, and Mg and R_2O is Li_2O, Na_2O, and K_2O, has been determined in [12]. The following composition (wt.%) is presented as an example: Bi_2O_3 — 87.55, TeO_2 — 4.74, SiO_2 — 2.40, ZnO — 2.11, SrO — 1.03, BaO — 0.61, and Li_2O — 1.19.

Thus it can be concluded that Bi_2O_3 can act as a glass-former with formation of a bismuth–titanium structural network of quite deformed octahedral groups $[BiO_6]$, though at low concentrations it acts as a modifier.

In summary, low-melting glasses which in combination with a luminophor form high-quality light-conversion coatings on substrates consisting of sheet glass at deposition temperature 650°C have been obtained in the experimental system.

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