

LOW-MELTING GLASSES DERIVED FROM THE PbO-B₂O₃-SiO₂ SYSTEM BY SUBSTITUTING ZnO FOR THE BASIC OXIDES

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The paper deals with the preparation and characterization of low-melting glasses derived from the PbO-B₂O₃-SiO₂ system by substituting ZnO for SiO₂ or PbO in the basic system. The basic system for the investigation was glass of the composition: 40 PbO, 34 B₂O₃, 26 SiO₂ (mol.%). Structural characteristics of the synthesized glasses were investigated by infrared spectroscopy. In addition, density, thermal expansion, crystallization ability and hydrolytic durability of the glasses were determined. The results show that the substitution of ZnO for PbO or SiO₂ in the base PbO-B₂O₃-SiO₂ system strongly affects all glass properties. The investigated glasses show a small tendency to crystallize, exhibit a good hydrolytic durability and the thermal expansion coefficients in the range $\alpha = (30 - 100) \times 10^{-7} \text{ K}^{-1}$.

INTRODUCTION

Low-melting oxide glasses with a high content of PbO are widely used as glazes and enamels [1,2]. Lately, the area of application of these glasses has been expanded to the fields of electronics and microelectronics (solder or sealing glasses, thick film capacitors and resistors, etc.) [3]. The bases for the development of these glasses are the PbO-B₂O₃-SiO₂, PbO-B₂O₃-ZnO and ZnO-B₂O₃-SiO₂ systems. In order to improve the physico-chemical characteristics, small amounts of Ti, Ba, Cd, Ta, Ge, Li and Al oxides are usually added to the denoted three-component systems.

Besides the low melting temperature ($< 1200^\circ\text{C}$) the glasses should have following properties:

1. Thermal expansion coefficient compatible with the other materials in the system.
2. Thermal stability preventing crystallization in the temperature interval of application.
3. Chemical stability that enables normal usage during the manufacturing process.
4. High electric resistance at the temperature of application.
5. Corresponding values of viscosity and surface tension, as well as other specific properties [4-12].

According to the available literature data, systematic investigations of the structural and physico-chemical characteristics of the denoted glasses have not been performed up to now. The basic data on these glasses can usually be found only in the patent literature. Because of

the possible wide application area, the glasses derived from the basic PbO-B₂O₃-SiO₂ system by substituting ZnO for SiO₂ or PbO were chosen for investigation.

EXPERIMENTAL PART

Glass of the composition 40 PbO, 34 B₂O₃, 26 SiO₂ (mol.%) was chosen as the starting glass for the investigations. This glass lies in the region of transparent glass in the phase diagram of the PbO-B₂O₃-SiO₂ system [13]. Two groups of glasses were used for the study. The first group was obtained by substituting ZnO for SiO₂ from the starting glass, and the second group by substituting ZnO for PbO. Table 1 shows the composition and designation of the glasses.

Preparation of the glasses

The glasses were prepared by the standard procedure of melting the previously homogenized mixture of Pb₃O₄, H₃BO₃, SiO₂, and ZnO in a zirconia crucible. Melting was performed in a laboratory electric chamber furnace. The melting temperature of the starting glass and the first group of glasses was 1000°C and for the second group 1100°C . The melted glasses were quenched in air by pouring into a 50 mm diameter steel mould.

Measurement of glass properties

The density of the prepared glasses was determined by the pycnometric method. The hydrolytic durability of the glasses at 100°C was determined on the ground sam-

Table 1. Composition of the glasses.

glass No.	Oxide											
	PbO			B ₂ O ₃			SiO ₂			ZnO		
	batched (mol.%)	analyzed* (wt.%)	analyzed* (wt.%)	batched (mol.%)	analyzed* (wt.%)	analyzed* (wt.%)	batched (mol.%)	analyzed* (wt.%)	analyzed* (wt.%)	batched (mol.%)	analyzed* (wt.%)	analyzed* (wt.%)
starting glass												
01	40	69.4	69.4	34	18.4	18.0	26	12.2	12.6	-	-	-
Group I												
02	40	68.4	68.3	34	18.2	18.0	17	7.8	8.1	9	5.6	5.6
03	40	67.2	67.8	34	17.9	17.6	9	4.1	4.2	17	10.5	10.4
04	40	66.6	66.6	34	17.6	17.4	-	-	-	26	15.8	15.9
Group II												
05	30	58.5	58.4	34	20.7	20.4	26	13.7	14.1	10	7.1	7.0
06	20	44.5	44.4	34	23.6	23.4	26	15.7	15.9	20	16.2	16.2
07	10	25.9	25.8	34	27.5	27.6	26	18.3	18.3	30	28.3	28.2
08	-	-	-	34	33.0	32.9	26	21.7	21.8	40	45.3	45.2

* Glasses were analyzed by AAS, gravimetric and volumetric methods.

ples. The thermal expansion coefficient was calculated from the Winkelmann and Schott equation [14]:

$$\alpha = \alpha_1 p_1 + \alpha_2 p_2 + \dots \alpha_n p_n = \sum \alpha_i p_i \quad (1)$$

α_i – averaged numerical characteristic of the partial coefficients of expansion of the oxides, p_i – content of oxides in glass (wt.%)

The structural characteristics of glasses were determined by IR spectroscopy (Perkin Elmer 780). Measurements were performed in the range 400 - 4000 cm⁻¹ (powdered glass + KBr). The crystallization ability was determined by the method of continuous cooling of glasses at low rates [14].

The samples were previously prepared by melting in platinum crucibles at $T = 800$ °C (ASTM 829-81 procedure). After one hour the furnace was turned off and the samples inside were cooled to room temperature. The samples obtained were then analyzed by X-ray diffraction. The Philips PW 170 diffractometer with CuK α and a graphite monochromator (measurement range [(2 θ) 4 - 65°] was used.

RESULTS

The spectral transmissivity curves of the glasses in the infrared region are presented in figure 1.

Figure 2 shows the dependence of the density of prepared glasses on the ZnO content.

The calculated values of the thermal expansion coefficient are given in table 2.

Table 2. Calculated thermal expansion coefficients of prepared glasses.

	glasses							
	01	02	03	04	05	06	07	08
α (10 ⁻⁷ K ⁻¹)	94.1	94.7	95.8	96.6	67.2	59.1	48.6	34.1

The plot of the hydrolytic durability of the glasses at 100 °C vs. ZnO content is shown in figure 3.

The results of determination of the crystallization ability showed that only three glasses crystallized during the experiment (continuous cooling of the samples at low rates): glass 04 from the first group and glasses 05 and 06 from the second group. The diffraction patterns of these glasses are presented in figure 4.

DISCUSSION

The characteristic absorption bands of the IR spectra are located in the wavenumber region 600 - 1500 cm⁻¹ (figure 1). The denoted bands, a weak one at 680 cm⁻¹ and two broad ones with maxima at about 1000 cm⁻¹ and

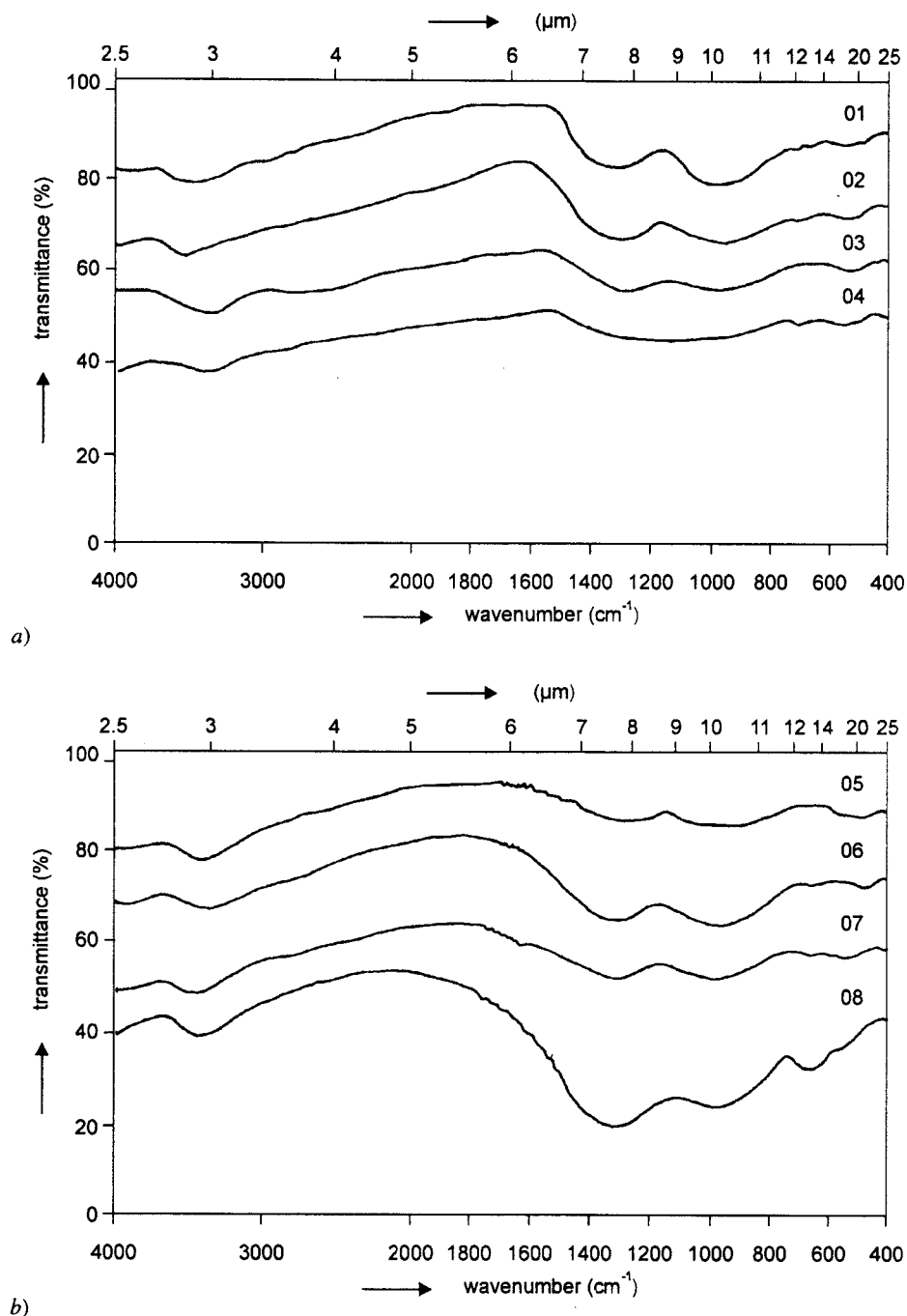


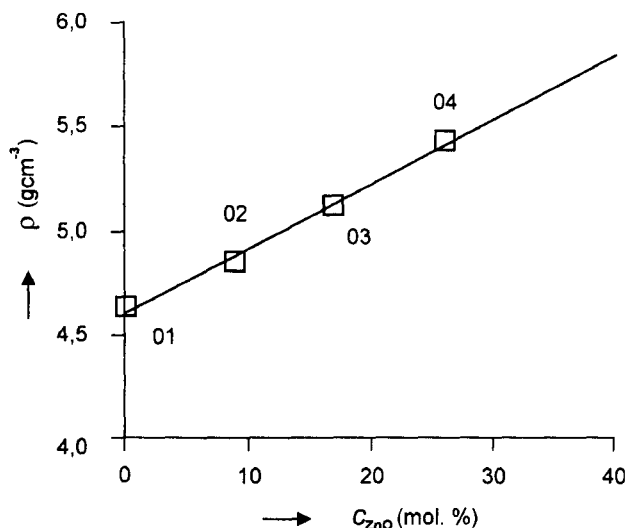
Figure 1. Infrared spectra of prepared glasses. a) glasses 01-04, b) glasses 05-08

1300 cm^{-1} respectively, correspond to the vibration of the oxygen bond to silicon and boron ions in the glass structure (tetrahedral SiO_4 , BO_3 and BO_4 groups).

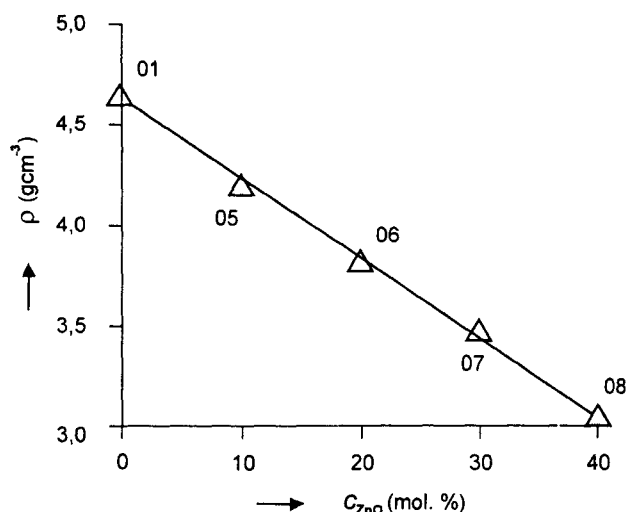
The introduction of ZnO into the starting glass does not cause any general change in the spectrum (there are no new peaks). The decrease in the intensity of the absorption bands until forming only one broad band (samples 03 and 04) is a consequence of the oxygen incorporation into the glass network due to the addition

of ZnO into the starting glass. The absorption band at 3400 cm^{-1} appearing in all the samples can be ascribed to the hydroxyl groups.

In the case of the glasses from the first group, which were obtained by substitution of ZnO for SiO_2 , there are no relevant changes of glass properties compared to the starting glass. The influence of introducing ZnO into the starting glass on the density is evident in the second group of glasses, which were obtained by substituting



a)



b)

Figure 2. The density of prepared glasses as a function of ZnO content.

a) – 01-starting glass; 02, 03, 04 - glasses derived from $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system by substitution of ZnO for SiO_2 ; b) – 05, 06, 07, 08 - glasses derived from $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system by the substitution of ZnO for PbO .

PbO with ZnO in the starting glass. The glass density decreases with decreasing PbO content (figure 2). The gradual substitution of ZnO for SiO_2 in the starting glass leads to a slight increase in the thermal expansion coefficient. On the other hand, the substitution of ZnO for PbO brings about a sudden drop of the α value.

It can be seen in figure 3 that the substitution of ZnO for SiO_2 , as well as of ZnO for PbO leads to an increased hydrolytic durability. The effect is more pronounced when ZnO is substituted for SiO_2 (the first group of glasses).

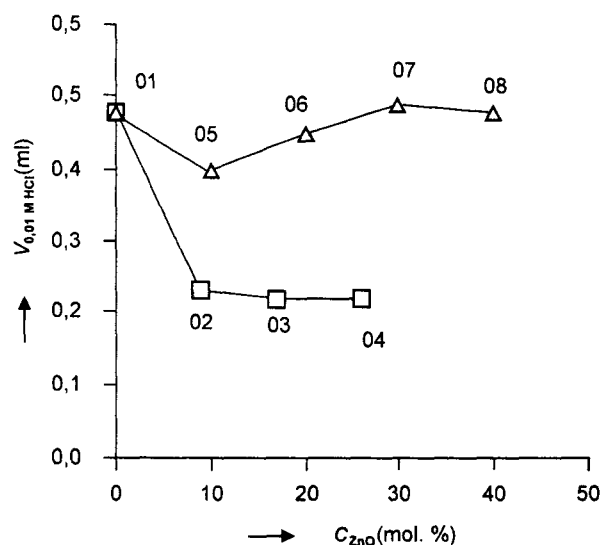


Figure 3. Hydrolytic durability of glasses at 100 °C vs. ZnO content.

The determination of the crystallization ability showed that the investigated glass systems are stable. Only three glasses, the glass from the first group obtained by completely substituting ZnO for SiO_2 and two glasses from the second series obtained by substituting 10 and 20 mol.% of ZnO for PbO , crystallized. Analysis of the diffraction patterns shows that the glassy phase is dominating in all three samples. The crystalline phase is present to a small extent. By comparing the obtained d -values to the standard ones, $3\text{ZnO} \cdot \text{B}_2\text{O}_3$ and $\text{PbO} \cdot \text{B}_2\text{O}_3$ (JCPDS - 27983 and 20575) were determined as the possible crystalline phases.

CONCLUSION

Low-melting glasses derived from the starting $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system by substituting ZnO for SiO_2 and PbO were investigated. The results of this investigation showed that the introduction of ZnO into the starting system considerably affects all the investigated properties of the prepared glasses.

The glasses show small tendency to crystallization, good hydrolytic durability and the thermal expansion coefficients in the range $\alpha = (30 - 100) \times 10^{-7} \text{ K}^{-1}$.

The properties of the glasses indicate their possible application in electronics and microelectronics (solder and sealing glasses, manufacture of condensers and resistors, etc).

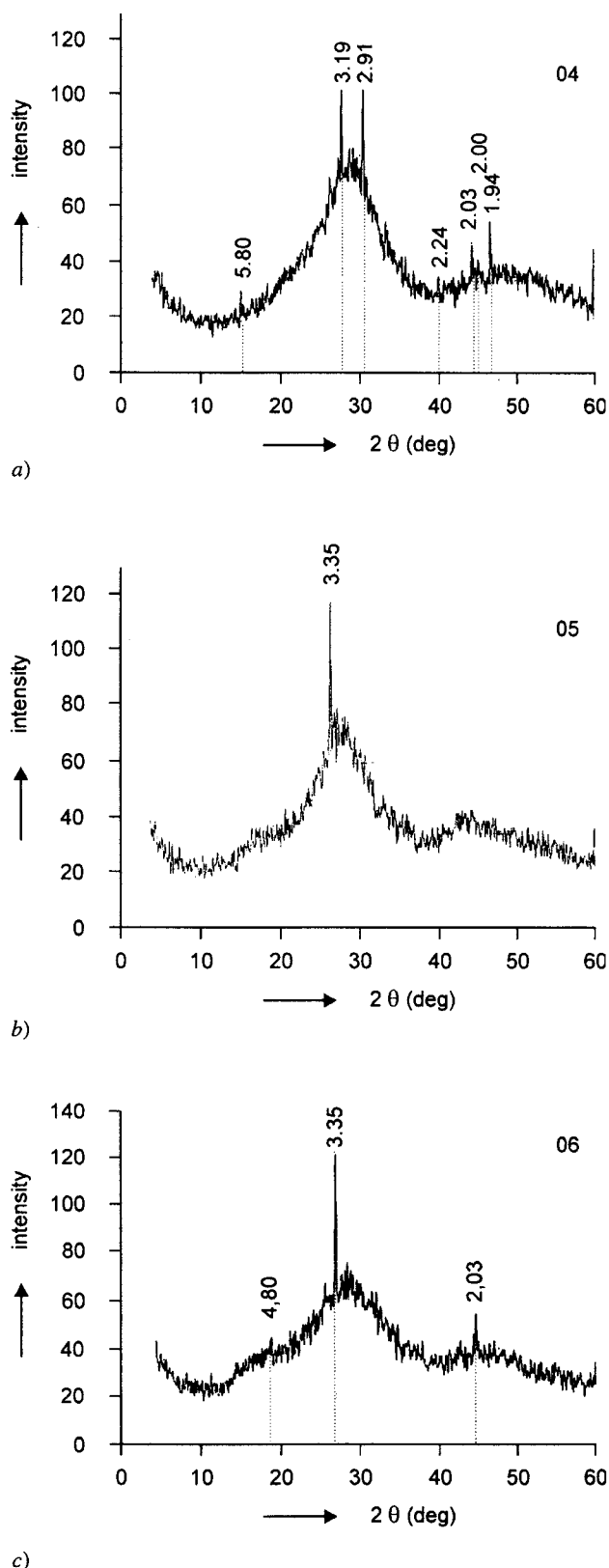


Figure 4. X-ray diffraction patterns of glasses a) – 04, b) – 05 and c) – 06.

References

1. V. Vargin V.: *Technology of Enamels*, McLaren and Sons Ltd., London 1967.
2. Harman C.: *Ceramic Glazes*, Cahners Book, Boston, Massachusetts 1973.
3. Harper C.A.: *Handbook of Thick Film Hybrid Microelectronics*, Book Company, New York 1974.
4. Berenznoi A.: *Sitali i Fotositali*, Mashinostroenie, Moskva 1981. (in Russian)
5. Berenznoi A., Kulmagov I.: *Neorganicheskie Materijali* 13, 1509 (1977). (in Russian)
6. Berenznoi A., Kulmagov I.: *Neorganicheskie Materijali* 14, 155 (1978). (in Russian)
7. Lee J., Perng J.: *Thermochimica Acta* 29, 161 (1990).
8. Lee J., Perng J.: *Glass Technol.* 77, 31 (1990).
9. USSR Patent No.1192295.
10. US Patent No. 3,759,727.
11. US Patent No. 3,533,832.
12. B. Chiou, R. West: *Cer.Bull.* 63, 816 (1984).
13. Mazurin O., Streltsina M.: *Properties of Glasses and Glass Forming Melts*, Vol II Izdatelstvo Nauka, Leningrad 1973.
14. Scholze H.: *Glas*, Springer Verlag, Heidelberg 1977.
15. Živanović V.: M.Sc.Thesis, Faculty of Technology and Metallurgy, University of Belgrade 1997.

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NÍZKOTAVITELNÁ SKLA ODVOZENÁ ZE SYSTÉMU $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ NÁHRADOU PbO NEBO SiO_2 OXIDEM ZINEČNATÝM

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V této práci byly předmětem studia skla odvozená ze systému $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ náhradou Zn za PbO nebo SiO_2 . Jako výchozí bylo zvoleno sklo složení PbO - 40, B_2O_3 - 34, SiO_2 - 26 (mol %).

První skupina těchto skel byla získána postupnou náhradou ZnO za SiO_2 ve výchozím skle, a druhá skupina náhradou ZnO za PbO. Skla byly připravována běžným postupem tavením homogenizované směsi Pb_3O_4 , H_3BO_3 a ZnO v zirkonoxidovém kelímku při teplotách 1000 a 1100 °C. Roztavené sklo se odlévalo a chladilo na vzduchu. Byly stanovovány fyzikální a vybrané fyzikálně chemické vlastnosti jako hustota, teplotní roztažnost, hydrolytická odolnost a krystalizační schopnost. Získané výsledky ukazují, že náhrada PbO nebo SiO_2 oxidem zinečnatým má značný vliv na všechny vlastnosti daného skla. Získaná skla mají výraznou odolnost proti rekrytalizaci, velmi nízkou vyluhovatelnost, a součinitel teplotní roztažnosti se pohybuje v mezích $\alpha = (30 - 100) \times 10^{-7} \text{ K}^{-1}$. Vzhledem k fyzikálně chemickým vlastnostem těchto nízkotavitelných skel lze uvažovat vývoj jejich využívání jako pájkových skel v elektronice a mikroelektronice.