Journal of Optoelectronics and Advanced Materials Vol. 6, No. 3, September 2004, p. 747 - 753

PHYSICAL PROPERTIES OF PbO-ZnO-P_2O_5 GLASSES II. REFRACTIVE INDEX AND OPTICAL PROPERTIES

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Phosphate glasses of composition x PbO – 10 ZnO - (90-x) P_2O_5, $30 \le x(\text{mol. \%}) \le 55$ (series A); 50 PbO –x ZnO – (50-x) P_2O_5, $0 \le x(\text{mol \%}) \le 20$ (series B); and x PbO – (60 – x) ZnO - 40 P_2O_5, $0 \le x(\text{mol \%}) \le 60$ (series C), were investigated. Experimental values of the refractive index (n) [$1.59 \le n \le 1.87$] were compared with the calculated values of n and good results were obtained using the Effective Medium Theory. Optical gap (E_g) varies in the region: $4.6 \le E_g[\text{eV}], 300\ \text{K} \le 4.98$, the temperature coefficient β of the optical gap was found around 6.7×10^{-4} [eV/K].

(Received April 27, 2004; accepted June 22, 2004)

Keywords: Phosphate glasses, Optical properties, Refractive index

1. Introduction

In previous communication [1] some interesting properties of PbO-ZnO-P_2O_5 glasses were briefly mentioned, see e.g., Refs. [2-5] in [1], and some structural properties of the three series of glasses were examined using both the infrared and Raman spectroscopy.

In this communication we continue with the study of physical properties of the three compositional series (A, B, C) of PbO-ZnO-P_2O_5 glasses [1]. Attention is given to the optical properties, namely to the refractive index and to the optical gap of these glasses.

2. Experimental

The studied glasses of PbO-ZnO-P_2O_5 system, see Table 1, were prepared by the way described in [1], where also the measurements of the basic physical properties is described [1].

The temperature dependence ($80 < T[K]) < 300$) of the optical transmission in the ultraviolet (UV) and visible (VIS) regions for some samples was measured using Beckman DU-640 spectrophotometer equipped with the optical cryostat Cryoson XL 500. The temperature dependence of the optical transmission at high temperatures ($300 < T[K] < \sim 600$) was measured for all the samples prepared using HP 8453 spectrophotometer equipped with the optical thermostat O.T.1 (R.M.I. Pardubice, Czech Republic). Thinner samples were prepared by a blowing technique (the thickness $d \sim 10^{-3}$ cm).

The reflectivity spectra were measured in the UV-VIS spectral region using Perkin-Elmer Lambda 12 spectrophotometer. The measurements were done on the flat natural surfaces of the bulk samples ($d \ge 0.4$ cm) prepared by a slow cooling of the melt. To depress and/or minimize any back

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reflection the backside of the samples was always roughened and finally darkened by a black absorbing paste. As the representative value of the refractive index (n), the geometric average $n = (n_R^2\ n_T)^{1/3}$, where $n_R = (1+R^{1/2})/(1-R^{1/2})$, $n_T = [1+(1-T^2)^{1/2}]/T$ values, were taken. Here T is the transmittivity, and R is the reflectivity of the sample, respectively. From the series of measurements we estimated the accuracy of the n-values determined in such a way around: $n \pm 0.06\ n$.

The values of the optical gap (E_g) were determined from the relation $(\alpha h\nu)^r \sim B^r(h\nu - E_g)$, where B is the slope of the short wavelength absorption edge, $h\nu$ is the incident photon energy, α is the absorption coefficient, and r – the power exponent, determines the type of the optical transition between the valence and conduction band. The best results were obtained for r = ½, that is for the Tauc´s edge [6]. The values of absorption coefficient were calculated using the relation:
$\alpha = 1/d \ln \{(1 - R)^2 + [(1 - R)^4 + 4\ R^2T^2]^{1/2}/2\ T\}$, see e.g. [7].

3. Results

Studied glasses of PbO-ZnO-P_2O_5 system represent three compositional series (A, B, C), whichever of is characterized:

A. Substitution of P_2O_5 by PbO, x PbO - 10 ZnO – (90-x) P_2O_5, $30 \leq$ x (mol.%) ≤ 55;
B. Substitution of P_2O_5 by ZnO, 50 PbO - x ZnO – (50-x) P_2O_5, $0 \leq$ x (mol.%) ≤ 20;
C. Substitution of ZnO by PbO, x PbO – (60 – x) ZnO - 40 P_2O_5, $0 \leq$ x (mol.%) ≤ 60.

The typical spectral dependencies of the absorption coefficient at room temperature for 3 different glasses studied, in $(\alpha h\nu)^{1/2}$ versus $h\nu$ coordinates, are shown in Fig. 1.

Estimated values of the optical gap are summarized in the Table 1. The optical gap values vary in rather narrow region from 4.6 eV (sample 9B) to 4.98 eV (sample 1A), and they are increasing with an increase in P_2O_5 content, see Table 1. The exception to this trend is the optical gap for the sample 15C. For constant P_2O_5 content ($[P_2O_5] = 40$), the optical gap seems to be mostly affected by a PbO content, as E_g decreases with increasing PbO content.

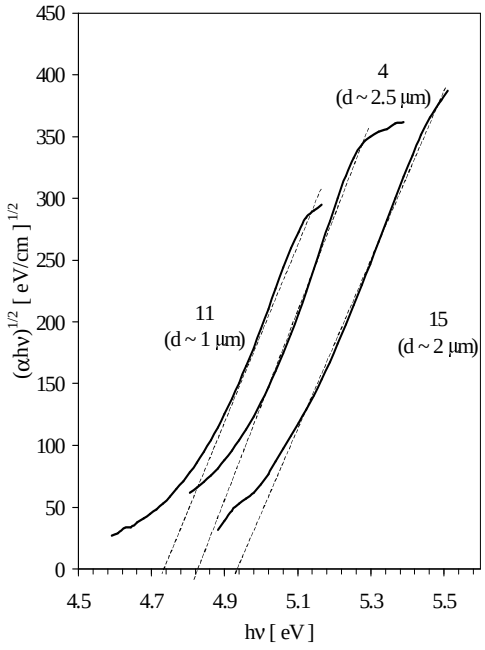

Fig. 1. The typical short wavelength edge in $(\alpha h\nu)^{1/2}$ vs. energy representation for the samples 4, 11 and 15, see Table 1. The number in parenthesis is the thickness of the sample.

The chemical composition of glasses studied together with some experimentally determined basic optical constants are summarized in the Table 1. For the reader´s convenience there are also listed the values of refractive index calculated using Lorentz-Lorenz equation (n_{LL}), the Effective Medium Theory (n_{EMT}) and the values of the non-linear refractive index (n_2), see 4.2, respectively. As evident from Table 1, the experimental refractive index (n) values are in the region $1.57 \leq n \leq 1.87$.

Table 1. Number of the sample (No(series)), the chemical composition, values of the optical (E_g), the temperature coefficient of the optical gap (β), see e.g. Fig. 2, the values of the experimental, and calculated refractive index using eqs. (1-6), respectively. By asterisk (*) the joint composition for all three series is marked.

No. (series)	Chem. comp. [mol %]			E_g [eV]	$\beta x10^4$ [eV/K]	n	n_{LL} (rel.error(%))	n_{EMT} (rel.error(%))	n_2x10^{12} [esu]
	PbO	ZnO	P_2O_5						
1(A)	30	10	60	4.98	8.46	1.58	1.69 (7.3)	1.62 (2.9)	0.80
2(A)	35	10	55	4.96	8.19	1.57	1.73 (10)	1.65 (5.1)	0.76
3(A)	40	10	50	4.93	5.68	1.66	1.78 (7.2)	1.68 (1.2)	1.50
4(A)	45	10	45	4.82	5.94	1.67	1.85 (10.5)	1.72 (2.7)	1.63
5(A,B,C)*	50	10	40	4.70	7.21	1.72	1.93 (11.3)	1.76 (1.6)	2.37
6(A)	55	10	35	4.62	7.06	1.74	2.01 (15.4)	1.80 (3.4)	2.57
7(B)	50	0	50	4.91	6.06	1.64	1.82 (7.2)	1.71 (0.5)	1.95
8(B)	50	5	45	4.71	5.91	1.77	1.87 (7.8)	1.73 (-0.5)	2.51
5(A,B,C)*	50	10	40	4.70	7.21	1.72	1.93 (11.3)	1.76 (1.6)	2.37
9(B)	50	15	35	4.60	6.79	1.75	1.98 (11.4)	1.79 (0.4)	3.23
10(B)	50	20	30	4.64	6.50	1.87	2.04 (8.9)	1.82 (-2.9)	5.55
11(C)	60	0	40	4.72	7.29	1.81	1.98 (9.8)	1.78 (-1.2)	3.77
5(A,B,C)*	50	10	40	4.70	7.21	1.72	1.93 (11.7)	1.76 (1.6)	2.37
12(C)	40	20	40	4.71	5.80	1.72	1.83 (6.3)	1.73 (0.3)	2.29
13(C)	30	30	40	4.63	6.24	1.65	1.82 (10)	1.70 (2.9)	1.41
14(C)	20	40	40	4.82	4.94	1.64	1.73 (5.5)	1.67 (1.8)	1.29
15(C)	10	50	40	4.93	5.44	1.62	1.65 (1.8)	1.64 (1.2)	1.12
16(C)	0	60	40	-	-	1.59	1.60 (0.2)	1.61 (1.1)	0.90

In Fig. 2 the typical $E_g(T)$ dependence is shown in the temperature region 80 – 600 K. Assuming the simplest E_g vs. T dependence in the form $E_g(T) = E_g(0) - \beta T$, from the high temperature part of $E_g(T)$ dependence, the values of the optical gap temperature coefficient β were determined, see Table 1.

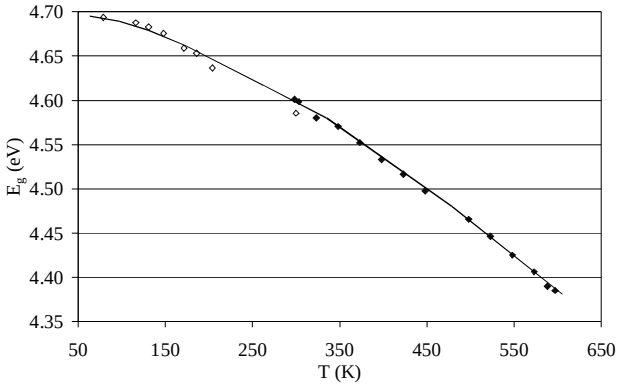

Fig. 2. Temperature dependence of the optical gap of 50PbO-15ZnO-35P_2O_5 glass.

The values of β in phosphate glasses studied are comparable to the β values observed usually in various semiconductors inclusive amorphous chalcogenides [8].

4. Discussion

4.1 Compositional dependencies of both the optical gap and the refractive index

In Figs. 3,4 the compositional trends of the optical gap (E_g), and the refractive index (n), are summarized for the reader´s convenience.

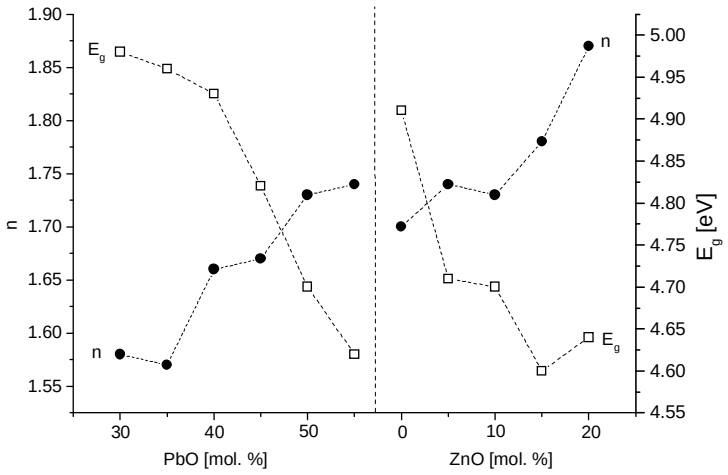

Fig. 3. The variation of the optical gap (□) and the refractive index (●) in xPbO-10ZnO–(90-x)P_2O_5 (A-series, left hand side) and 50PbO-xZnO–(50-x)P_2O_5 (B-series, right hand side) glasses. The dashed lines are only guides for the eyes.

It is evident from Fig. 3 that formal substitution of P_2O_5 by PbO or ZnO has similar consequencies, with a decrease in P_2O_5 content the values of E_g decrease and the values of n increase as the content of PbO or ZnO increases. The decrease in E_g values could be explained using the concept of additivity of local gaps [9] ($E_g(P_2O_5 \approx 6$ eV [11], E_g(PbO) = 2.73 eV [10], and E_g(ZnO) = 3.26 eV [11]).

In our previous paper [1], the structural changes in glasses studied were observed in the Raman and in the infrared spectra and in compositional dependencies of another properties, e.g. an increasing density accompanied by an increasing of the glass transition temperature, in A- and B-series of glasses [1]. All the mentioned features indicate a depolymerization of the virgin phosphate network and shorter phosphate chains formation [1]. An increase in refractive index with increase in both the PbO content and ZnO content (Fig. 3) reflects an increase in both the density and the overall polarizability of an actual phosphate network in accordance with general expectation, that the adding of highly polarizable ions to the glass-network causes a significant increase in refractive index values. Polarizable species, such as Pb^{2+} retard the light propagation through the phosphate glass, as does the conversion of bridging oxygen to non-bridging oxygen. Hence, PbO as heavy metal oxide has more polarizable effect then ZnO and its effect on the properties is more distinct. For ultraphosphate glasses (glasses 1A and 2A, see Table 1), the value of the refractive index is nearly constant ([ZnO] ≤ 10 mol %). The reason for such behavior is caused by transferring of $(Q^3+Q^2)^*$ starting structure to long Q^2 chains, where both the PbO and ZnO have mainly the roles of modificators of a phosphate network. Further adding of PbO evokes the formation of chains with

* For explanation Q^3, Q^2, Q^1, see e.g. [1]

different lengths, i.e. more non-bridging oxygens are formed and refractive index can increase. In the case of B-series of glasses, the starting composition 50PbO-50P_2O_5 consists of long lead-metaphosphate chains. The embedding of the first 5 mol% ZnO can be schematically described by the pseudo-reaction according to $Q^2 + ZnO \rightarrow 2\ Q^{1\,*}$. Hence, the number of non-bridging oxygens increases and the refractive index increases also.

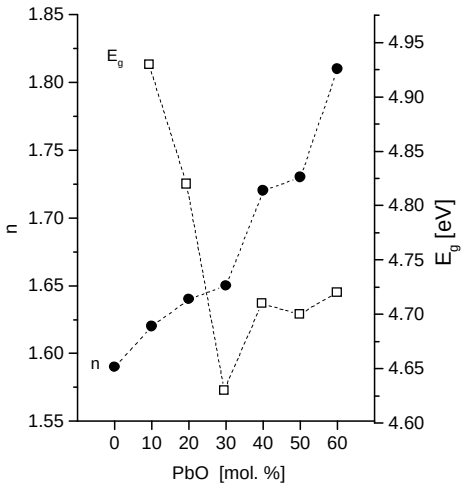

Fig. 4. The variation of the optical gap (□) and the refractive index (●), of glasses xPbO-(60–x)ZnO-40 P_2O_5.The dashed lines are only guides for the eyes.

Of interest is compositional dependence of C-series of glasses studied, i.e. glasses where PbO substitutes ZnO. It is evident from Fig. 4, that sequential addition of PbO has dramatic effect on the optical parameters observed. The refractive index increases rather monotonously up to ~ 30 mol% PbO, but E_g value drops to a minimum just at ~ 30 mol% PbO.

When more PbO is going to substitute ZnO, the refractive index steeply increases with a break between 40-50 mol% PbO up to n = 1.82 (60 PbO-40 P_2O_5). The E_g value increases with a break from the virgin E_g = 4.63 eV (30 PbO-30 ZnO- 40 P_2O_5) up to E_g = 4.71 eV (40 PbO-20 ZnO- 40 P_2O_5) and further addition of PbO has nearly no effect on the value of E_g.

Previous study of the same glasses [1] indicate that a nano-scale phase decomposition in glasses with content PbO ~ 30-40 mol% can proceed see also [12]. Further substitution of PbO for ZnO ([P_2O_5] = 40 mol%) means that PbO is built in the network partly decomposed into nano-scale separated entities $Pb_2P_2O_7$ and $Zn(PO_3)_2$. These ones could react with PbO and form, in hierarchy of phosphate glasses, the higher entities, e.g. tetraphosphates ($(Pb_{5/6}Zn_{1/3})_3P_4O_{13}$). Hence, PbO acts as a glass-former and optical gap remains nearly constant. Refractive index is very sensitive property to the presence of polarizable ions, and a change from pyro- to polyphosphate structure is seen in Fig. 4 as a break. Results presented in Fig 4 are in harmony with the results of our previous study [1].

4.2. Calculation of the refractive index

The refractive index in isotropic materials, e.g. liquids, glasses, cubic crystals, is usually expressed by the Lorentz-Lorenz equation [13]

$$R_m = [(n^2 - 1)/(n^2 + 1)]V_m, \quad (1)$$

where R_m is the molar refraction, V_m is the molar volume, and n is the refractive index. The molar refraction can be expressed [13] as a function of a molecule polarizability (α_m) [14]:

$$R_m = 4\pi\alpha_m(N_A/3) = 2.52\alpha_m\,, \qquad \alpha\ [Å^3] \tag{2}$$

where N_A is Avogadro's number. The molecule polarizability in the first approximation is additive quantity, and e.g. for an oxide A_iO_q it can be expressed by the relation [13]:

$$\alpha_m = i\ \alpha_i + q\ \alpha_O{}^{2-}\,, \tag{3}$$

where α_i, $\alpha_O{}^{2-}$ is the polarizability of cation and anion (oxygen(2-)), respectively.

Assuming that for our ternary glasses, the molar refraction is additive quantity, we obtain:

$$R_{m,t} = \sum f_i R_{m,i}\,, \tag{4}$$

where $R_{m,t}$ is molar refraction of ternary glass, f_i is molar fraction of the i-th oxide and $R_{m,i}$ is the molar refraction of the i-th oxide. Using tabulated α_i, $\alpha_O{}^{2-}$ values, see e.g. [15,16], we calculated α_m and $R_{m,t}$ values, and finally from rel.(1), the refractive index values n_{LL} were calculated.

For mixtures or alloys the refractive index can be, however, calculated using the "Effective Medium Theory" (EMT), which in fact results from the Maxwell-Garnet theory [17] extended for multicomponent mixtures in Ref. [18]. For dielectric constant of a mixture (ε_m) composed by i-th components with dielectric constant ε_i, it is valid [17]:

$$\sum_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} y_i = 0 \tag{5}$$

where $\varepsilon_{i,m} = (n_{i,m})^2$ and y_i is the volume fraction of the i-th component. Using the known values of refractive index (n(PbO)=2.35, n(ZnO)=1.98, and $n(P_2O_5)$=1.48), using the experimental values of density of studied glasses presented in [1], Table 1, and using known values of the densities of binary components ($\rho(PbO) \cong 9.53$ g/cm^3, $\rho(ZnO) \cong 5.61$ g/cm^3 , $\rho(P_2O_5) \cong 2.39$ g/cm^3), we calculated ε_m and n_m values for studied glasses. For reader's convenience the experimental refractive index values (n), the refractive index values calculated according to Lorentz-Lorenz equation (n_{LL}), and refractive index values calculated according to EMT (n_{EMT}) are summarized in the Table 1, together with relative errors (rel.error(%) = 100(n_{LL}, n_{EMT} – n)/n). From the Table 1 it is evident that EMT gives better overall agreement between calculated and experimental values, as the relative error varies in the region –2.9 < rel.error (%) < 5.1, contrary to LL relation where relative error varies in the region 0.2 < rel.error (%) < 15.4. It should, however, be noted that both the LL or EMT can be used only for rough estimation of refractive index in studied glasses. In using LL method, in fact, we neglected changes of polarizability in α_i and $\alpha_O{}^{2-}$ induced by structural changes which accompany the changes in the chemical composition. Unfortunately, the relevant data are not available. In using EMT also only the changes in V_m are taken into consideration while the properties of PbO, ZnO and P_2O_5 are taken to be constant in the whole composition region. (Hence, quite good agreement between n_{EMT} and n cannot be overestimated).

Finally, using the semiempirical relation [19]

$$n_2\ [\text{esu}] = 2.6 \times 10^{-13}(n^2 - 1)^4/n\,, \tag{6}$$

the calculated values of non-linear refractive index (n_2) are summarized also in the Table 1. The calculated n_2 values are of order magnitude higher than n_2 for SiO_2 glass and, hence, these glasses could be promising for construction of some non-linear electro-optical devices.

5. Conclusions

Three series of colourless PbO-ZnO-P_2O_5 glasses with the values of the optical gap 4.6 – 4.98 eV, were prepared. The temperature coefficient of the optical gap (β) was found in the region:

$8.46 \times 10^{-4} < \beta$ [eV/K] $< 4.94 \times 10^{-4}$. The values of the experimental refractive index (n) increases from n = 1.57 for 35 PbO- 10 ZnO- 55 P_2O_5 to n = 1.87 for 50 PbO-20 ZnO-30 P_2O_5. The chemical composition of the glasses studied covers structural richness of phosphate glasses from ultraphosphate up to polyphosphate glasses.

For a constant content of P_2O_5 the substitution of ZnO by PbO leads to an increase in the network disorder. At the chemical composition close to 40 PbO-20 ZnO-40 P_2O_5 where the clear minimum in E_g(PbO) dependence and a break/change in the slope n(PbO) dependence, is observed, we speculate, that some nano-phase separation could be responsible for a decrease in the overall network connectivity. This idea is supported by our previous study of these glasses [1], where in T_g(PbO) the minimum was observed, too. Within the error in the region (–2.9) – (+5.1) % the compositional dependence of the refractive index for all 16 glasses could be described using the simplest version of "Effective Medium Theory".

Rather high optical gap, good chemical stability of studied glasses, especially for the content P_2O_5 < 40 mol%, rather low glass-transition temperatures and convenient refractive index values ($1.57 \le n \le 1.87$) makes the glasses interesting for optical applications. The promising also seems to be estimated value of non-linear refractive index $n_2 \approx 5.6 \times 10^{-12}$ [esu] for 50 PbO- 20 ZnO–30 P_2O_5.

Acknowledgements

We acknowledge the support from the research project VZ 253100001 of the Czech Ministry of Education. L.T. acknowledges also support from the Key project ASCR 2050602 and from FWO Vlaanderen (Belgium).

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