

Some properties of $(\text{PbO})_x(\text{ZnO})_{15}(\text{P}_2\text{O}_5)_{85-x}$ glasses

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Eight glasses were prepared along the line $(\text{PbO})_x(\text{ZnO})_{15}(\text{P}_2\text{O}_5)_{85-x}$. An increase in the density ($3.23 \leq \rho [\text{g/cm}^3] \leq 5.42$), in the glass transition temperature ($278 \leq T_g [^\circ\text{C}] \leq 372$), in the refractive index ($1.56 \leq n \leq 1.79$), and a decrease in the optical gap ($5.39 \geq E_g [\text{eV}] \geq 4.65$), respectively, was observed with an increase in PbO content. Raman spectra of glasses studied give evidence for phosphate network depolymerisation due to substitution of P_2O_5 by PbO. The temperature (T) dependence of the optical gap ($E_g(T)$) in the region $300 < T[\text{K}] < 600$ was determined and approximated by a simple linear relation ($E_g(T) = E_g(T \rightarrow 0) - \gamma T$) with the temperature coefficient (γ) of the optical gap in the region $4.91 \leq \gamma \times 10^4 [\text{eV/K}] \leq 6.55$, respectively.

(Received January 5, 2007; accepted January 15, 2007)

Keywords: Phosphate glasses, Raman spectroscopy, Optical properties

1. Introduction

Phosphate glasses stabilised with some heavy metal oxides are suitable for construction of modern optical devices. Attention is given to the systems where the most important properties of phosphate glasses are conserved, namely low melting temperature, high values of thermal expansion coefficient, low glass transition temperature (glass to metal seals [1-3]), high optical transmission starting from UV region, solubility of rare earth elements (various optical elements [4]), and, simultaneously, good chemical stability. Liu et al. [1-3] found that ZnO in amount around 15 mol % is sufficient for phosphate glass stabilisation from water corrosion and PbO behaves as a glass-modifier and/or glass-former in dependence on its concentration. In fact, both PbO and ZnO incorporated into a phosphate matrix improve the chemical stability of resulting glasses [1 - 8, and Refs. cited therein where also various properties of the PbO - ZnO - P_2O_5 glasses were studied]. Recently we studied $(\text{PbO})_x(\text{ZnO})_{10}(\text{P}_2\text{O}_5)_{90-x}$ glasses ($30 \leq x \leq 55$) [9]. We found that substitution of P_2O_5 by PbO is accompanied by an increase in the glass-transition temperature and in the refractive index, and by a decrease in the average molar volume (V_M) of glasses prepared. It was suggested that substitution of P_2O_5 by PbO leads to a fragmentation and depolymerization of phosphate network; nevertheless, T_g values increase with an increase in PbO, because of P-O-Pb(Zn) linkages assist to the network cross-linking. In this communication we focus our attention to the preparation and physical properties of $(\text{PbO})_x(\text{ZnO})_{15}(\text{P}_2\text{O}_5)_{85-x}$ where the content of ZnO equal to 15 mol % represents an upper limit for conservation of ZnO behaviour mainly as the network modifier [1, 4]. Attention is also given to estimation of the optical gap and its temperature dependence from the room temperature up to temperature close to the glass-transition temperature.

2. Experimental

The glasses of the series $(\text{PbO})_x(\text{ZnO})_{15}(\text{P}_2\text{O}_5)_{85-x}$ ($x = 15 - 50$ mol. %, with the step of 5 mol. %), were prepared using a two step melting technique and subsequent quenching, the method recently used for preparation of $(\text{PbO})_x(\text{ZnO})_{10}(\text{P}_2\text{O}_5)_{90-x}$ glasses [10]. Glassy (confirmed by XRD analysis), colourless and well transparent samples were obtained. Glasses prepared were stored in desiccator filled with dry argon to preclude the hydrolysis mainly of ultraphosphate glasses ($x = 15, 20, 25, 30$, see Table 1). The chemical composition of glasses prepared was verified using microprobe X-ray analysis (JEOL JSM 5500 LV) with a precision $\pm 1.5\%$ in atomic fraction of elements. The details of the measurements of the density, the dilatometric glass transition temperature, and Raman spectra, were similar to those reported recently [11].

For optical transmission measurements the samples with the average thickness $d \approx 15 \mu\text{m}$ were prepared by a blowing method. The optical transmission was measured in the region $300 < T[\text{K}] < 600$ in the optical thermostat O.T.I. (R.M.I., Czech Republic) placed into the sample compartment of HP 8453 spectrophotometer, respectively. The measurements were done after perfect stabilisation of the temperature. The reflectivity spectra in the UV-VIS spectral region were measured using PE Lambda 12 spectrophotometer. The bulk samples with the thickness around 0.5 cm, on one side polished to an optical quality and on the opposite side roughened and covered by a black paste to minimize a “back side reflection”, were used. The absorption coefficient (α) was calculated using the relation [12]:

$$\alpha = (1/d) \ln \{ (1-R)^2 + [(1-R)^4 + 4R^2 T^2]^{1/2} / 2T \}, \quad (1)$$

where T is the transmission and R is the reflectivity. In the first approximation we assume nearly invariant R with

both the temperature and the wavelength within the spectral region of the absorption edge. This assumption introduces an error in E_g estimation up to $\pm 5\%$. Owing to the thickness of the samples prepared ($d \approx 15\ \mu\text{m}$) our transmission spectra are relevant to absorption processes associated mainly with the Urbach edge ($\alpha \leq 10^3\ \text{cm}^{-1}$). Hence, the values of the optical gap we estimated according to relation [13]:

$$\alpha = \alpha_0 \exp(\hbar\omega/\Delta E) = (10^3\ \text{cm}^{-1}) \exp[(\hbar\omega - E_g)/\Delta E], \quad (2)$$

where ΔE is the slope of Urbach edge and $E_{03} = \hbar\omega$ for b $\alpha = 10^3\ \text{cm}^{-1}$ is taken as a measure of the optical gap. Refractive index values were estimated as an geometric average $n = (n_R^2 n_T)^{1/3}$, where $n_R = (1 + R^{1/2})/(1 - R^{1/2})$ and $n_T = [1 + (1 - T^2)^{1/2}]/T$, where both R and T were measured in the well transparent region. From series of measurements we estimated the accuracy of n values estimated in this way better than: $n = \pm 0.06n$ for the wavelength $\lambda \approx 800\ \mu\text{m}$.

3. Results and discussion

3.1. Structural characterisation

The structure of glasses was characterised by Raman spectroscopy. In Fig. 1 are shown Raman spectra of selected glasses under study. Raman features (R_F) observed are similar to those found in another similar phosphate glasses [11]; (i) The highest frequency R_F observed at around $1280\ \text{cm}^{-1}$ ($x = 15$) we tentatively assign to possible overlap of weak asymmetric stretching motion of non-bridging oxygen in $Q^{2,**}$ phosphate tetrahedra and symmetric $\text{P}=\text{O}$ stretch on Q^3 tetrahedra [11]. Here we assume that symmetric $\text{P}=\text{O}$ stretch on Q^3 tetrahedra is shifted to lower frequency because π -bond delocalisation. With a decrease content of P_2O_5 the Q^3 tetrahedra are diminished and for the chemical composition where $x = 35$ the highest frequency R_F seen at $\nu \sim 1250\ \text{cm}^{-1}$, is due to weak asymmetric stretching motion of non-bridging oxygen in Q^2 phosphate tetrahedra. (ii) The R_F at around $1140\ \text{cm}^{-1}$, ($15 \leq x \leq 35$), we assign to symmetric PO_2 stretch on Q^2 tetrahedra. Most probably owing to an increase content of PbO incorporated into phosphate network this R_F is shifted to lower frequency (around $1110\ \text{cm}^{-1}$ for $x = 50$, respectively). (iii) Simultaneously, with an increase in content of PbO ($x = 45, 50$) new R_F appears at around $1030\ \text{cm}^{-1}$ which one we attribute to PO_3 stretch on Q^1 tetrahedra [11]. Such evolution in Raman features indicates considerable depolymerisation of phosphate network. This is in harmony with a decrease in relative intensity of R_F in the region $670\ \text{cm}^{-1}$ ($x = 15$) to $740\ \text{cm}^{-1}$ ($x = 50$) origin of which one we assign to symmetric stretching motion of bridging oxygen ($\nu_s(\text{P}-\text{O}-\text{P})$) connecting neighbouring

tetrahedra in Q^2 chains [1, 3, 4]. (iv) The lowest frequency R_F at around $130\ \text{cm}^{-1}$, seen for $x \geq 0.35$, is unambiguous evidence of PbO -bonds vibrations. We note that such R_F was observed in the Raman spectra of lead silicate, lead borate and lead gallate glasses [14] and also in lead phosphate glasses [15]. Moreover, as shown recently [16] the most intensive R_F of both α (tetragonal) and β (orthorhombic) modifications of PbO appears just at around $143\ \text{cm}^{-1} - 145\ \text{cm}^{-1}$. (v) An origin of the last R_F observed at around $350\ \text{cm}^{-1}$ remains to be unclear. Some weak and broad R_F is seen for all Raman spectra, see Fig. 1; the intensity of this R_F increases with an increase in PbO content. Hence, one is tempting to assign this R_F to formation of tetragonal PbO pyramids with Pb(II) at the apex, [16, 17]. In such case the PbO_4 tetrahedra can be incorporated into the phosphate network in corner sharing arrangement and formation of $\text{P}-\text{O}-\text{Pb}$ linkages assists to network cross-linking. Consequently, lead oxide behaves as a network former and owing to formation of $\text{P}-\text{O}-\text{Pb}$ linkages an increase in glass-transition temperature can be expected. Indeed, see Table 1, substitution of P_2O_5 by PbO is accompanied by an increase in T_g .

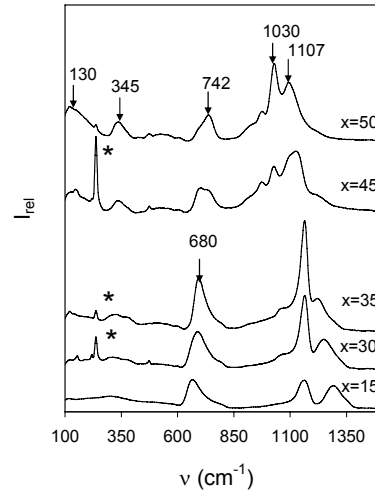


Fig. 1. Raman spectra of selected $x\ \text{PbO}-15\ \text{ZnO}- (85-x)\ \text{P}_2\text{O}_5$ glasses; ultraphosphate ($x = 15, 30$), metaphosphate ($x = 35$), and polyphosphate glasses ($x = 45, 50$), respectively. (By * are signed the measurement artefacts).

However, the R_F at around $350\ \text{cm}^{-1}$ can be assigned to the bend mode of phosphate polyhedra with zinc modifier [4] and also to $\text{O}-\text{P}-\text{O}$ bending band [2]. Hence, unambiguous assignment of R_F seen at around $350\ \text{cm}^{-1}$ remains to be an open question.

3.2. Some physical characteristics of the investigated glasses

The experimental values of some physical properties of glasses under study are summarised in Table 1. It is evident that substitution of P_2O_5 by PbO leads to a decrease in both the molar volume and optical gap while the glass-transition temperature, the density and the refractive index increase, respectively. Hence, the trend in compositional changes in T_g , ρ and V_M , E_g and n is similar

** Q^n tetrahedral structural units; n is number of bridging oxygens, hence, Q^2 unit has two bridging and two non-bridging oxygens [4, 11].

to that one found for $(\text{PbO})_x (\text{ZnO})_{10}(\text{P}_2\text{O}_5)_{90-x}$ glasses [18]. Role of PbO on the optical properties of phosphate glasses is well known. Increase in PbO content of a glass leads to an increase of both the density and average polarisability of a glass network, hence, refractive index should increase. For example in $(\text{PbO})_x (\text{ZnO})_{0.6-x}(\text{P}_2\text{O}_5)_{0.4}$ glasses the refractive index increases from $n(x=0) \approx 1.58$ to $n(x=0.6) \approx 1.81$ [19].

It is well known that lead oxide can be incorporated into phosphate network as a network modifier and/or as a network former. Consequently, the intrinsic short wavelength absorption threshold or the optical gap should be influenced by PbO [20]. For example in $(\text{PbO})_x(\text{P}_2\text{O}_5)_{1-x}$ glasses the optical gap decreases from $E_g(x=0.3) \approx 4.5$

eV to $E_g(x=0.55) \approx 4.2$ eV. From Table 1 it is clear that compositional change in both the refractive index and optical gap are nearly monotonous. Hence, we can estimate the optical gap of studied glasses using the concept of a simple alloying model [21]:

$E_g = \sum y_i E_{g,i}$, where y_i and $E_{g,i}$ are the formal volume fraction and the optical gap of the i th component of the glass, respectively. Calculated E_g values, assuming $E_g(\text{PbO}) = 2.6$ eV [17], $E_g(\text{ZnO}) = 3.1$ eV [22], $E_g(\text{P}_2\text{O}_5) = 6$ eV (tentatively used value), $\rho(\text{PbO}) = 8.7$ g/cm³, $\rho(\text{ZnO}) = 5.6$ g/cm³, $\rho(\text{P}_2\text{O}_5) = 2.4$ g/cm³, are shown in Table 1, column 8.

Table 1. Sample chemical composition, the dilatometric glass transition temperature (T_g), the hydrostatic density (ρ), the molar volume ($V_M = M/\rho$, M is the average molar weight, respectively), the experimental ($E_{g,\text{exp}}$, 300 K) and calculated ($E_{g,\text{calc}}$, 300 K) optical gap values, and the experimental (n_{exp} (800 nm)) and calculated (n_{LL}), (n_{EMT}) values of the refractive index, see rels. (3), (4).

Chem. composition [mol%]			T_g [°C]	ρ [g/cm ³]	V_M [cm ³ /mol]	$E_{g,\text{exp}}$ [eV]	$E_{g,\text{calc}}$ [eV]	n_{exp}	n_{LL}	n_{EMT}
PbO	ZnO	P ₂ O ₅								
15	15	70	278	3.23	44.89	5.39	5.59	1.56	1.55	1.56
20	15	65	296	3.37	44.26	5.23	5.48	1.58	1.57	1.59
25	15	60	314	3.59	42.69	5.38	5.36	1.61	1.60	1.62
30	15	55	323	4.07	39.63	5.16	5.23	1.64	1.62	1.65
35	15	50	340	4.13	38.07	4.95	5.10	1.67	1.65	1.68
40	15	45	343	4.58	36.10	5.10	4.95	1.70	1.68	1.72
45	15	40	361	4.98	33.96	4.85	4.78	1.74	1.72	1.76
50	15	35	372	5.42	32.00	4.65	4.60	1.79	1.76	1.81

The agreement between calculated and experimental values seems to be acceptable since the difference $dE_g = E_{g,\text{exp}} - E_{g,\text{calc}}$ values does not exceed $\pm 0.04 E_{g,\text{exp}}$.

The refractive index of glasses is usually expressed using Lorentz-Lorenz [23] relation:

$R_M = [(\epsilon - 1)/(\epsilon + 2)]V_M$, where $\epsilon = n^2$ is the dielectric constant and the molar refraction (R_M) is assumed to be additive quantity: $R_M = \sum y_i R_{M,i}$. After simple arrangement we can write for refractive index of a multi-component glass:

$$n_{\text{LL}} = \left\{ 1 + 3 \sum y_i (\epsilon_i - 1) / (\epsilon_i + 2) / [1 - \sum y_i (\epsilon_i - 1) / (\epsilon_i + 2)] \right\}^{1/2}, \quad (3)$$

where $n_i = \sqrt{\epsilon_i}$ is the refractive index of the i th component of the glass, respectively. Alternatively, for mixtures or alloys the refractive index can be expressed also using the simplest version of “Effective Medium Theory” (EMT) based on Maxwell-Garnet approach [24] and extended for multi-component in [25]:

$$\sum y_i (\epsilon_i - \epsilon_m) / (\epsilon_i + 2\epsilon_m) = 0, \quad (4)$$

where $n_{\text{EMT}} = n_m = (\epsilon_m)^{1/2}$ is the refractive index of our glasses. Using the values of refractive index $n(\text{PbO}) = 2.35$, $n(\text{ZnO}) = 1.98$ and $n(\text{P}_2\text{O}_5) = 1.48$, we calculated n_{LL} and n_{EMT} values, see Table 1, columns 10,

11. Agreement between experimental and calculated values of refractive index seems to be reasonable since for n_{LL} we found $n_{\text{exp}} - n_{\text{LL}} \leq +0.02 n_{\text{exp}}$, and for n_{EMT} - $n_{\text{exp}} - n_{\text{EMT}} \leq -0.012 n_{\text{exp}}$. Reasonable correspondence between the experimental and calculated (by simple averaging) values of both the optical gap and refractive index indicates that these quantities are mainly influenced by the chemical composition of the glasses examined. There are no indications of jump like changes in $E_g(x)$ and $n(x)$ dependencies which could indicate some step like changes in the network structure of glasses studied. The substitution of P_2O_5 by PbO leads to change of ultraphosphate network into polyphosphate network as indicated by Raman spectroscopy.

3.3. Temperature dependence of the optical gap

In Fig. 2 the typical spectral dependence of the short wavelength absorption edge for temperatures $T > 300$ K, is shown. Absorption coefficient (α) for $\log \alpha < 3$ obeys “Urbach Rule”, see rel. (2), with an almost parallel red shift of the edge induced by temperature increase. Temperature dependence of the optical gap ($E_g(T) = E_{03}(T) = \hbar\omega(T)$ for $\alpha(T) = 10^3$ cm⁻¹) for two selected glasses is shown in Fig. 3. The experimental data (solid circles) were fitted by simple linear relation:

$$E_g(T) = E_g(0) - \gamma T; \quad (5)$$

where $E_g(0)$ is the optical gap at $T = 0$ K and γ is the temperature coefficient of the optical gap. Estimated values of $E_g(0)$ ($= E_{g(0)LR}$) and γ are displayed in columns 4 and 5 in Table 2. It is known that linear fit to $E_g(T)$ overestimates true $E_g(0)$ value. Recently, in some $\text{PbO-ZnO-P}_2\text{O}_5$ glasses, inclusive some of $(\text{PbO})_x(\text{ZnO})_{10}(\text{P}_2\text{O}_5)_{90-x}$ glasses, the temperature dependence ($80 \leq T[\text{K}] \leq 600$) of the optical gap on thin samples ($d \approx 2\mu\text{m}$) was examined [26].

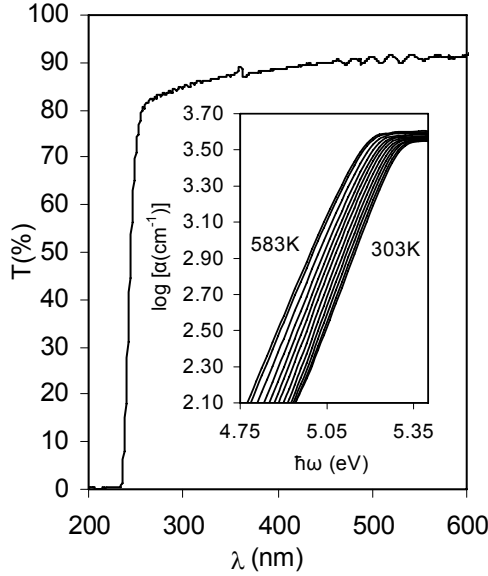


Fig. 2. Spectral dependence of the optical transmission of glassy 30PbO-15ZnO-65P₂O₅ (300 K); in the inset the short wavelength absorption edge in the temperature region ~ 300 K–600 K is shown.

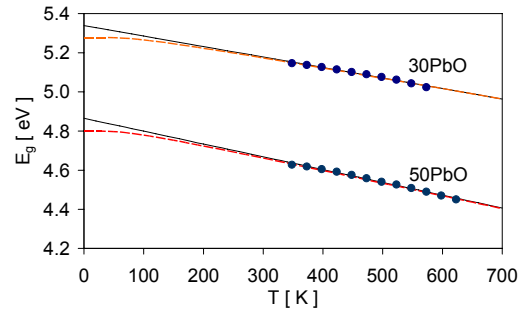


Fig. 3. Temperature dependence of the optical gap of the samples with 30 mol. % PbO and 50 mol. % PbO, respectively. By full circles are marked the experimental data (~ 300 – 600 K), full line-linear approximation, see text, dashed curve-fit to rel.(6).

It was found that for all studied glasses Fan's one-phonon approximation [27]:

$$E_g(T) = E_g(0) - A / [\exp(\hbar\omega_{ph} / k_B T) - 1], \quad (6)$$

here A is a material constant, k_B is Boltzmann constant, and $\hbar\omega_{ph}$ is the mean energy of phonons involved in the absorption process, respectively, fits the experimental data quite well. The values of the mean phonon energy for glasses examined in [26] were found in the region $0.017 \leq \hbar\omega_{ph} [\text{eV}] \leq 0.025$ which correspond to phonon frequency in the region 137 cm^{-1} to 202 cm^{-1} , the frequency close to phonon activity of PbO in phosphate glasses [28,29]. We assume that for our glasses similar values of $\hbar\omega_{ph}$ are valid and, despite absence of low temperature data, we tried to estimate $E_g(0)$ values using Fan's one-phonon approximation. Typical fits of our experimental $E_g(T)$ values are shown by dashed curves in Fig. 3 and calculated $E_g(0)$ ($= E_{g(0)Fan}$), A and $\hbar\omega_{ph}$ values are summarised in columns 6, 7, 8, respectively, in Table 2.

Table 2. Optical parameters for glasses studied; optical gap at $T = 0$ K ($E_g(0) = E_{g(0)LR}$ estimated by linear relation, γ is temperature coefficient of $E_g(T)$ dependence, the values A , $\hbar\omega_{ph}$, and $E_g(0)$ ($= E_{g(0)Fan}$) - fitting parameters, see (5), respectively.

Chemical composition [mol%]			$E_{g(0)LR}$ [eV]	$\gamma \times 10^4$ [eV ⁻¹]	Fitting parameters, rel. (5)		
PbO	ZnO	P ₂ O ₅			A [eV]	$\hbar\omega_{ph}$ [eV]	$E_{g(0)Fan}$ [eV]
15	15	70	-	-	-	-	-
20	15	65	5.42	4.91	0.10	0.017	5.38
25	15	60	5.56	5.16	0.13	0.018	5.54
30	15	55	5.34	5.36	0.13	0.018	5.28
35	15	50	5.11	5.20	0.11	0.018	5.06
40	15	45	5.26	4.62	0.10	0.019	5.21
45	15	40	5.03	5.78	0.12	0.018	4.97
50	15	35	4.87	6.55	0.13	0.018	4.80

Estimated $E_{g(0)Fan}$ values correspond quite well to the $E_{g(0)Fan}$ values found for close chemical compositions in [26]. Comparing the optical gap values and its temperature dependencies in $(\text{PbO})_x(\text{ZnO})_{15}(\text{P}_2\text{O}_5)_{85-x}$ glasses and in

glasses examined in [26] we suppose that both the values of the optical gap and its temperature dependence are mainly influenced by PbO content.

4. Conclusions

In the present study the density, the molar volume, the glass transition temperature, the refractive index, Raman spectra, and also the temperature dependence of the short wavelength absorption edge of glasses $(\text{PbO})_x(\text{ZnO})_{15}(\text{P}_2\text{O}_5)_{85-x}$, where $15 \leq x \leq 50$, were examined. Raman spectra reveal of the ultraphosphate network fragmentation as PbO content increases. It is suggested that the PbO_4 tetrahedra can be incorporated into the phosphate network in corner sharing arrangement and formation of P-O-Pb linkages assist to network cross-linking. Indeed with an increase content of PbO the glass-transition temperature increases. Compositional changes of both the refractive index and optical gap values were fitted using simple alloy models indicating an absence of some gross step like structural changes in the network of glasses studied.

Good transparency in a part of ultraviolet and visible spectral region (4.65 ($x = 15$) $< E_g[\text{eV}] < 5.39$ ($x = 50$)) together with reasonable values of refractive index (1.56 ($x = 15$) $< n < 1.79$ ($x = 50$)) and low glass-transition temperature (278 ($x = 15$) $< T_g [^\circ\text{C}] < 372$ ($x = 50$)) makes these glasses interesting for various optical applications.

Acknowledgements

This work is supported by VZ 0021627501 of the Czech Ministry of Education. L.T. acknowledges also support from the project AVOZ 40500505. We acknowledge M.Vlček for kind measurements of Raman spectra.

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