REFRACTIVE INDEX OF GLASSES
IN THE PbO-ZnO-P$_2$O$_5$ SYSTEM

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Ten glasses of PbO–ZnO–P$_2$O$_5$ system have been prepared. The experimental values of refractive index of these glasses were compared with the theoretical ones calculated using (i) Lorentz–Lorenz equation, (ii) Virtual Crystal Approximation (VCA), and (iii) Effective Medium Theory (EMT). It is shown that the refractive index determined by EMT and VCA follows the experimental values of refractive index quite well and these methods can be used for prediction of the refractive index values in PbO–ZnO–P$_2$O$_5$ system glasses. It is also supposed that the non-linear refractive index value could reach the value $n_2[esu] \approx 5.4 \times 10^{-12}$ for glasses with the linear refractive index $n > 1.8$.

Introduction

Glasses have emerged as an important class of materials for modern devices because their optical constants and other physical and chemical parameters can be

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controllably adjusted.

Refractive index (n) is one of the most important basic optical constant of glass. To obtain glasses with a higher ($n > 1.7$) or high ($n > 2$) refractive index, the optimum compositions need to be selected in such a way that highly polarizable cations (like a Pb^{2+}) are incorporated into glassy matrix with as many as possible network formers and/or network modifiers in the glass.

In the case of lead-zinc phosphate glasses, the Pb^{2+} cations have a mixed role depending on the concentration of Zn^{2+}. At low concentration of both cations, they are rather modifiers of the phosphate network, at high content of ZnO and/or PbO, Pb^{2+} is a rather network former [1,2]. The $PbO-ZnO-P_2O_5$ glasses posses interesting physico-chemical properties, e.g. good chemical durability [1], low melting temperature and high fluidity [3]. Their structure was studied using Raman (e.g. in Refs.[2,4,5]), infrared (e.g. in Refs. [5–7]) and nuclear magnetic resonance ((NMR), e.g. in Refs.[2,4,8,9]) spectroscopies. All known properties make these glasses attractive for a variety of applications, e.g. for glass-to-metal sealing [3] or as potential material for storage of nuclear wastes [10]. The $PbO-ZnO-P_2O_5$ glasses are transparent from UV-region, see e.g. [11], and are promising for photonic applications as fibre lasers, and e.g. as non-linear optical elements [2,11].

This communication describes the preparation and properties of 10 glasses from $PbO-ZnO-P_2O_5$ system and compares the experimentally estimated values of the refractive index with the theoretical ones calculated using various non-common ways of refractive index prediction.

Experimental

The glasses studied were prepared from the oxides PbO, ZnO (purity > 97 %, Aldrich), and H_3PO_4 (85 %, p.a., Lachema Brno) in a Pt-crucible. The stoichiometric amounts of oxides and H_3PO_4 (diluted with distilled water) were mixed and heated for ~ 3 hours in the region 20 – ~ 500 °C. In the next step, the oxides obtained were heated and melted at temperatures ~ 1050 °C for about 20 min. Then the melt was poured onto a stainless plate at room temperature to obtain glassy (confirmed by XRD analysis), colourless and transparent samples.

The density (d) of the glasses was determined using standard hydrostatic method described in Ref. [11].

The reflectivity spectra were measured in the ultraviolet and visible (UV-VIS) spectral region using Perkin-Elmer Lambda 12 spectrophotometer on the thick samples (the thickness $t \geq 0.4$ cm) with naturally reflecting surface. The backside of the samples was always roughened and darkened by black absorbing paste to depress and/or minimize any back reflection.

The optical transmission in UV-VIS spectral region was measured on the samples of various thickness ($t \sim 10^{-3} - 10^{-1}$ cm) using the HP 8453

spectrophotometer. Thinner samples were prepared by a blowing technique $(t \sim 10^{-3}$ cm).

Results and Discussion

The glasses under study represent typical glasses from the $PbO-ZnO-P_2O_5$ system, they are colourless, transmitting from the UV-region. In Fig. 1 the typical spectral dependence of transmittivity and reflectivity of glassy $50\,PbO-20\,ZnO-30\,P_2O_5$ is shown.

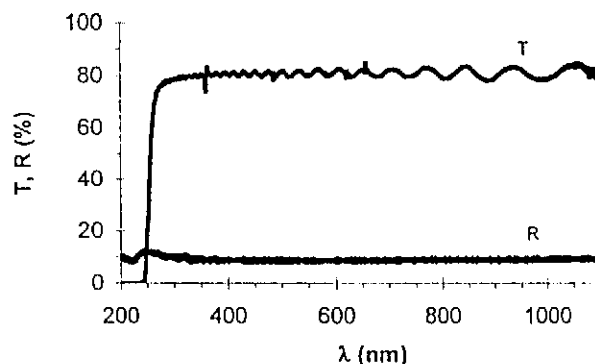Fig. 1 Spectral dependence of the transmittivity (T, sample thickness $t \sim 20$ μm) and reflectivity (R) of glassy $50\,PbO-20\,ZnO-30\,P_2O_5$

Estimation of the Experimental Values of Refractive Index

The values of refractive index (n_R, n_T) were estimated from

(i) reflectivity (R) in the transparent region where $n_R = (1 + R^{1/2})/(1 - R^{1/2})$, and (ii) transmission measurements (T) in the transparent region where $n_T = [1 + (1 - T^2)]^{1/2}/T$.

In the case of the samples with naturally reflecting surface (without mechanical and chemical polishing), where sometimes density fluctuations exist, the experimental values of refractive index were estimated as a geometrical average ($n_{g.a.}^{'}$) with accent to reflectivity R

$$n_{g.a.} = \left(n_T n_R^2\right)^{1/3} \qquad (1)$$

Calculation of the Theoretical Values of the Refractive Index

In glasses, because of the lack of crystal periodicity, the conventional theoretical methods that work for perfect crystals should be used with some caution. In the field of oxide glasses the methods often used for calculation of refractive index were discussed in Ref. [12]. In principle, all the calculations are based on assumption of additive equation, i.e. the linear combination (LC) of refractive index of the components (oxides) present

$$n_{LC} = \sum n_i f_i \tag{2}$$

where n_i is the partial refractive index of the i-th component (oxide) of a glass and f_i is the molar fraction of the i-th component ($\sum_i f_i = 1$). For better agreement between the calculated and experimental values various corrections have been used, see e.g. [13–15]. The other method used for calculation of the values of refractive index is based on the Lorentz–Lorenz equation, see e.g. [16]

$$R_m = \left(\frac{n_0^2 - 1}{n_0^2 + 1} \right) \frac{M}{d} \tag{3}$$

where R_m is the molar refraction, n_0 is the refractive index, d is the glass density, M is molar weight, and hence $M/d = V_m$ is the molar volume of the glass.

It is well known (see e.g. [17]) that molar refraction can be expressed as a function of polarizability (α_m) of a molecule

$$R_m = 4\pi\alpha_m \frac{N_A}{3} = 2.52\,\alpha_m, \qquad \alpha\ [\text{Å}^3] \tag{4}$$

where N_A is Avogadro's number. According to Ref. [16] the polarizability of molecule, α_m, is additive quantity, and hence α_m for an oxide $A_i O_q$ is given by relation

$$\alpha_m = i\alpha_i + q\alpha_{O^{2-}}$$

where α_i is the polarizability of cation and $\alpha_{O^{2-}}$ is the polarizability of oxide ion. For our ternary glasses we assume additivity of the molar refractions

$$R_m = \sum f_i R_{m_i} \tag{5}$$

where f_i is molar fraction of the i-th oxide and R_m is the molar refraction of the i-th oxide. Consequently, using published α_i, $\alpha_{O^{2-}}$ values (e.g. [18,19]) one can calculate R_m and α_m values, and finally the refractive index

$$n_0 = \left(\frac{2M + 1}{1 - M} \right)^{1/2}, \quad M = \frac{R_m}{V_m} \tag{6}$$

In alloy-like semiconductor systems two methods are often used for calculation of the refractive index. The first method results from the "Virtual Crystal Approximation" (VCA) [20], and it was successfully used also in the field of non-crystalline chalcogenides [21,22]. It is based on the configurational approach and can be used to study order/disorder in solid solutions. In the most straightforward variant two or more pseudoatoms are placed at a given site and these ones, occupying the same site, do not interact with each other. The system can be taken as a regular solution, the compositional dependence or theoretical value of the refractive index in glassy alloys can be calculated using relation

$$\varepsilon_{alloy} = \sum y_i \varepsilon_i \pm \Pi_i \gamma_i \tag{7}$$

where γ_i is the bowing parameter which equals to zero for an ideal solution, ε_i is the dielectric constant of the i-th component, and also $\varepsilon_i = n_i^2$ and $\varepsilon_{alloy} = n_{alloy}^2$. The other method for calculation of the dielectric constant and, consequently, the refractive index, is based on the "Effective Medium Theory" (EMT) which in fact results from the Maxwell–Garnet theory [23] extended for multicomponent mixtures in Ref. [24]. For dielectric constant of the i-th component of mixture (ε_m) of i- components (oxides) it is

$$\sum_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} y_i = 0 \tag{8}$$

where ε_m is the dielectric constant of a mixture, y_i is the volume fraction of the i-th component and also $\varepsilon_i = n_i^2$ and $\varepsilon_m = n_m^2$.

We calculated the values of refractive index using the methods mentioned above, i.e.:

Table I The input values of dielectric constant ε, molar weight M, density d, molar refraction R_m, molar polarizability α_m, for PbO, ZnO and P_2O_5 used in the calculation of theoretical refractive index

Oxide	n_i	ε_i	M_i, g mol^{-1}	d_i, g cm^{-3}	R_{mi}, cm^3 mol^{-1}	α_{i}, Å^3
PbO	2.35	5.52	223.19	8.	17.824	7.073
ZnO	1.98	3.92	81.39	5.6	7.295	2.895
P_2O_5	1.48	2.19	141.94	2.39	17.134	6.792

Note: α_m(PbO, ZnO) values were calculated from the relevant α_i, $\alpha_{O^{2-}}$ values given in Ref. [18], the α_m(P_2O_5) was calculated from α_i, $\alpha_{O^{2-}}$ values given in Ref. [19]. R_{mi} values for oxides were calculated according to relation (3) using α_{mi} values, see the last column of Table I.

(i)   Lorentz–Lorenz formula (n_{LL}),
(ii) VCA (n_{VCA}), and
(iii) EMT (n_{EMT}).

The input values, ε, M, d, R_m, α_m for the oxides used are summarised in Table I.

Table II compares, for all the glasses prepared, the experimental values of refractive index ($n_{exp} = (n_R^2 n_T)^{1/3}$), the calculated n_{LC}, n_{LL}, n_{VCA}, n_{EMT} values, and the values of the relative errors (the numbers in parenthesis). For the reader's convenience the calculated values of refractive index together with n_{exp} values are plotted versus n_{exp} values in Fig. 2. It can be seen from Table II that the values of refractive index are influenced mainly by the content of PbO. When the content PbO increases, and simultaneously, the content of ZnO decreases and the content of P_2O_5 is constant, the value of refractive index increases, too.

The agreement between n_{exp}, n_{VCA} and n_{EMT} is reasonable, indicating that both n_{VCA} and n_{EMT} could be used for a prediction of refractive index in a multicomponent systems which behave as alloys. It is also seen that the simple EMT approach better correspond to the experimental values of refractive index than the VCA approach. Nevertheless, the mean value of relative errors in both these cases are smaller than ~ 3 % (see Table II, the data in parenthesis); the deviation between experimental and theoretical values corresponds with the experimental error of our way of the refractive index estimation. The Lorentz–Lorenz equation for calculation of the values of refractive index is less useful in our case (the mean relative error is ~ 7 %, see Table II). Finally, we note that for the glassy sample of composition $(PbO)_{50}(ZnO)_{20}(P_2O_5)_{30}$ it is $n_{exp} \approx 1.87$; the non-linear refractive index (n_2) calculated using the semiempirical relation [25]

Table II Number of the sample, chemical composition and density, the values of experimental refractive index (n_{exp}) estimated using Eq. (1); the theoretical refractive index calculated by LL (n_{LL}, Eqs (3) – (6)), VCA (n_{VCA}, Eq.(7)), and EMT (n_{EMT}, Eq.(8)), together with the values of relative error of all the methods used

Chem. comp. (in mol %) PbO–ZnO–P$_2$O$_5$	Density, g cm^{-3}	n_{exp}	n_{LC} (rel. error, in %)	n_{LL} (rel. error, in %)	n_{VCA} (rel. error, in %)	n_{EMT} (rel. error, in %)
1: 50 – 0 – 50	4.64	1.7	1.92 (–12.6)	1.82 (–7.2)	1.76 (–3.4)	1.74 (–2.3)
2: 50 – 5 – 45	4.86	1.74	1.94 (–11.6)	1.87 (–7.8)	1.78 (–2.5)	1.76 (–1.4)
3: 50 – 15 – 35	5.41	1.78	1.99 (–11.8)	1.98 (–11.8)	1.84 (–3.37)	1.82 (–2.2)
4: 50 – 20 – 30	5.6	1.87	2.02 (–7.5)	2.04 (–8.9)	1.87 (0)	1.85 (–1.1)
5: 40 – 10 – 50	4.31	1.66	1.88 (–13.1)	1.78 (–7.2)	1.73 (–3.9)	1.71 (–2.9)
6: 60 – 0 – 40	5.37	1.81	2.0 (–10.8)	1.98 (–9.8)	1.84 (–1.8)	1.82 (–0.8)
7: 50 – 10 – 40	5.1	1.73	1.97 (–13.9)	1.93 (–11.6)	1.81 (–4.6)	1.79 (–3.5)
8: 40 – 20 – 40	4.63	1.72	1.93 (–11.8)	1.83 (–6.3)	1.78 (–2.9)	1.76 (–1.9)
9: 10 – 50 – 40	3.55	1.62	1.82 (–12.2)	1.65 (–1.8)	1.66 (–2.4)	1.65 (–1.7)
10: 0 – 60 – 40	3.2	1.59	1.78 (–11.9)	1.60 (–0.2)	1.61 (–1.4	1.61 (–1.1)
Value of the mean error			11.7	7.3	2.6	1.7

$$n_2[esu] = 2.6 \times 10^{-13} \frac{(n_0^2 - 1)^4}{n_0} \tag{9}$$

reaches the value $n_2[esu] = 5.4 \times 10^{-12}$ (n_0 is the linear refractive index) which is one order of magnitude higher than n_2 for SiO$_2$ glass.
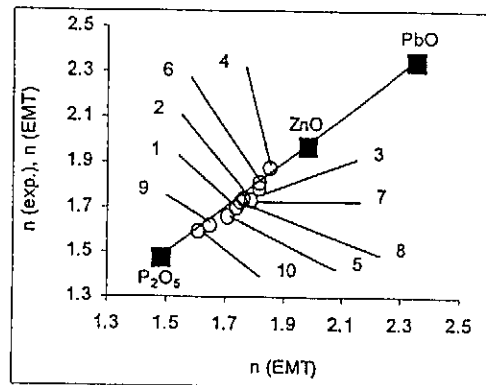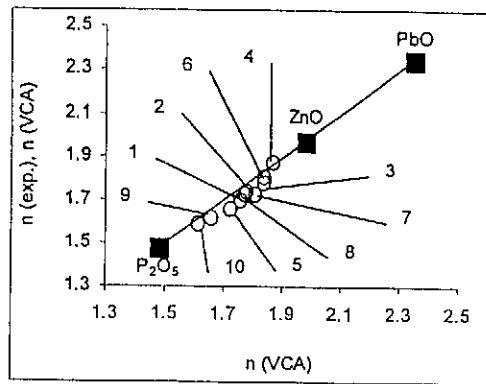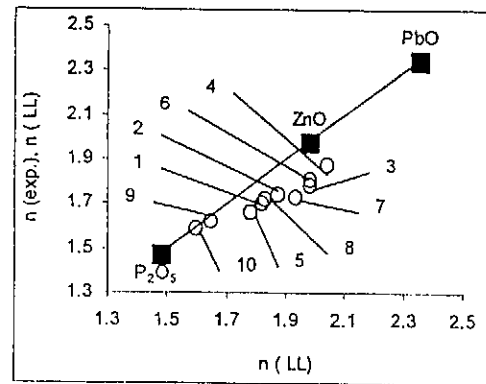
Fig. 2 Dependence of the experimental and theoretical values of refractive index (n) calculated from (i) Lorentz–Lorenz equation (Eq.(6)), (ii) Virtual Crystal Approximation (Eq.(7)), (iii) Effective Medium Theory (Eq.(8)). Full line – the calculated versus calculated n-values, open circles are marked with the sample number and correspond to experimental n-values, while full squares are n-values of the relevant oxides, see Table I.

Conclusion

All the prepared and studied glasses of $PbO-ZnO-P_2O_5$ system are colourless with the experimental refractive index varying from 1.59 to 1.87.

The refractive index mainly increases with increasing PbO content. As satisfactory agreement has been obtained between the experimental values of refractive index and the calculated ones using only The Effective Medium Theory and Virtual Crystal Approximation.

We also predict that the glasses with a higher refractive index ($n > 1.8$) could reach the non-linear refractive index one order of magnitude higher than SiO_2 glass.

Acknowledgements

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