

# On the structure and optical band gap in some $(\text{PbO})_x(\text{BaO})_{0.3-x}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$ glasses

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Four quaternary yellowish and well transparent glasses were prepared. The structural arrangement of the glasses was examined by Raman scattering and no gross structural changes were found due to substitution of BaO by PbO. The glass transition of the glasses prepared was found in the region 300 °C ( $x = 0.2$ ) to 343 °C ( $x = 0.05$ ), the refractive index was found in the region 1.9<sub>5</sub> ( $x = 0.05$ ) to 2.1<sub>5</sub> ( $x = 0.2$ ) and the optical band gap was found in the region 3.58 eV ( $x = 0.2$ ) to 3.75 eV ( $x = 0.05$ ).

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## 1. Introduction

Glasses based on TeO<sub>2</sub> have been widely studied for their promising properties including the low glass-transition temperature, high refractive index, transparency from visible to near infrared spectral region, and high non-linear refractive index, see e.g. [1-4]. Attention has also been paid to TeO<sub>2</sub> based glasses containing heavy metal oxides (HMO) [5-7]. Binary and ternary glasses TeO<sub>2</sub>-ZnO, TeO<sub>2</sub>-PbO [8] and TeO<sub>2</sub>-ZnO-BaO [9] have recently been studied. In all the cases, see e.g. [8, 9] with an increase in the content of modifiers the distortion of TeO<sub>4</sub> structural units (s.u.) leading to formation of TeO<sub>3</sub> s.u. is suggested. In the glasses TeO<sub>2</sub>-PbO prepared by slow cooling several crystalline compounds such as PbTeO<sub>3</sub>, Pb<sub>2</sub>Te<sub>3</sub>O<sub>8</sub> and TeO<sub>2</sub>, were found. The cut-off wavelength for TeO<sub>2</sub>-ZnO glasses was found at around 350 - 360 nm while for TeO<sub>2</sub>-PbO glasses it was found at around 397 - 407 nm. In the glasses TeO<sub>2</sub>-ZnO-BaO it is suggested that BaO improves the thermal stability of the glasses, increases the glass-transition temperature and increases the Raman gain. Attention was also paid to HMO quaternary TeO<sub>2</sub> based glasses for instance PbO-ZnO-B<sub>2</sub>O<sub>3</sub>-TeO<sub>2</sub> glasses [10]. It has been suggested that the basis in these glasses is a lead-tellurium lattice where the main Te based s.u. are TeO<sub>3</sub> pyramids independently from the chemical composition. The presence of two glass-forming oxides (B<sub>2</sub>O<sub>3</sub> and TeO<sub>2</sub>) in these glasses in all probability leads to their microheterogeneous structure of which the origin is liquation [10]. In this paper we report on the structural consideration and optical band gap of new PbO-ZnO-BaO-

TeO<sub>2</sub> glasses to certain aspects as an analogue to PbO-ZnO-B<sub>2</sub>O<sub>3</sub>-TeO<sub>2</sub> glasses.

## 2. Experimental

The glasses  $(\text{PbO})_x(\text{BaO})_{0.3-x}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$  where  $x = 0.05, 0.1, 0.15$  and  $0.2$  were prepared from the corresponding oxides PbO, ZnO, TeO<sub>2</sub> and BaCO<sub>3</sub> (purity 99.95%, Sigma Aldrich). The mechanical mixture of the components in the corresponding stoichiometric ratio, with a total weight 20 g, was thoroughly homogenized in a covered Pt crucible and melted for approximately 30 min at the temperature 850 °C. The melts were stirred three times, poured onto polished nickel plate preheated to the temperature  $T \approx 200$  °C and slowly cooled down to the ambient temperature. Yellowish and well transparent glassy samples, as confirmed by the absence of diffraction patterns, were prepared. The chemical composition was verified by an X-ray analysis (JEOL JSM 5500 LV) with an accuracy  $\pm 1.5$  at% of an element. The hydrostatic density ( $\rho$ ) was determined by the Archimedean method and the values of the molar volume  $V_{m,\text{exp}}$  were obtained using the relation:  $V_{m,\text{exp}} = M/\rho$ , where  $M$  is the molar weight of the glass.

The values of the coefficient of the thermal expansion (CTE) were estimated from the low temperature expansion curve of the glasses and the dilatometric glass-transition temperatures ( $T_g$ , TMA) were estimated using the standard intercept method employing thermomechanical analysis (TMA). The glass-transition temperatures ( $T_g$ , DTA) and the crystallization temperatures ( $T_c$ ) were estimated from

the preliminary differential thermal analysis (DTA) measurements [11]. The  $T_g$  values were estimated as an inflex and the maximum of the observed exo-peaks as the  $T_c$  values.

The Raman spectra were recorded using the Fourier Transform Infrared spectrometer (FTIR) Bruker model IFS 55 equipped with FRA 106 Raman module in back scattering geometry using a Nd:YAG laser beam (excitation light wavelength  $\lambda = 1064$  nm, slit width = 4  $\text{cm}^{-1}$ , laser power  $\approx 300$  mW at the sample surface). All the Raman spectra were taken at a room temperature using 200 scans on the bulk sample with a flat natural optical surface. The Bose-Einstein correction has been applied to the spontaneous Raman scattering data.

Optical transmission in UV-VIS spectral region was measured on the samples prepared by glass blowing. The samples with a thickness  $d = 2 - 3$   $\mu\text{m}$  were used. Certain details of the optical transmission (T) and reflectivity (R) measurements have been described recently [12]. Optical band gap values ( $E_g$ ) were determined, assuming non-direct optical transitions, from the relation:  $(Kh\nu)^{1/2} = B^{1/2}(h\nu - E_{g,\text{non}})$ , where  $E_{g,\text{non}}$  is the non-direct optical band gap,  $B^{1/2}$  the slope of the short wavelength absorption edge (SWAE) reflects the sample disorder [13],  $h\nu$  is the photon energy and K is the absorption coefficient calculated using the relation [14]:

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

### 3. Results and discussion

The chemical composition (x), the density ( $\rho$ ), the experimental molar volume ( $V_{m,\text{exp}}$ ), the additive molar

volume ( $V_{m,\text{add}}$ ),  $\Delta V (= V_{m,\text{add}} - V_{m,\text{exp}})$ , the dilatometric glass-transition temperature ( $T_g$ , TMA), the glass-transition temperature ( $T_g$ , DTA) and the crystallization temperatures ( $T_{c1}$ ,  $T_{c2}$ ) are summarized in Table 1. We have noted that for all the glasses the exo-peak namely at around  $T_{c2}$  is quite broad indicating in all probability the complicated character of the crystallization process. We shall restrict our consideration of DTA results only to the fact that the presence of at least two crystallization processes ( $T_{c1}$ ,  $T_{c2}$ ), indicating the possible complicated structural arrangement of the glasses were observed and leaving further discussion of this problem to more directed DTA experiments.

It is apparent in Table 1 that with an increase in PbO content the density increases and the values of the glass-transition temperature decrease. Both these results correspond to the fact that a less dense BaO is substituted by a more dense PbO and simultaneously the overall cohesive energy of the network decreases because (i) the bond dissociation energy (E) of the BaO bond is higher than the bond energy of the PbO bond ( $E(\text{BaO}) \approx 560$   $\text{kJmol}^{-1} > E(\text{PbO}) \approx 380$   $\text{kJmol}^{-1}$  [15]), and (ii) in all probability the entropy increases since the network of the glasses is composed of several structural units corresponding to several possible compounds which exist in the binary systems PbO-TeO<sub>2</sub>, BaO-TeO<sub>2</sub> and ZnO-TeO<sub>2</sub>. The indirect indication of the presence of certain complicated structural units is illustrated (i) by the fact that  $V_{m,\text{exp}} < V_{m,\text{add}}$ , that is by certain densification of the glasses proceeded, and (ii) by the existence of at least two crystallization processes at around  $T_{c1}$  and  $T_{c2}$  [11].

Table 1. The chemical composition (x), the density ( $\rho_{\text{exp}}$ ), the experimental molar volume ( $V_{m,\text{exp}}$ ), the additive molar volume ( $V_{m,\text{add}}$ ),  $\Delta V (= V_{m,\text{add}} - V_{m,\text{exp}}$ ), the dilatometric glass-transition temperature ( $T_g$ , TMA), the DTA glass-transition temperature ( $T_g$ , DTA) and the crystallization temperatures ( $T_{c1}$ ,  $T_{c2}$ ) of the studied  $(\text{PbO})_x(\text{BaO})_{0.3-x}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$  glasses.

x, PbO	$\rho_{\text{exp}}$ , ( $\text{gcm}^{-3}$ )	$V_{m,\text{exp}}$ , ( $\text{cm}^3\text{mol}^{-1}$ )	$V_{m,\text{add}}$ , ( $\text{cm}^3\text{mol}^{-1}$ )	$\Delta V$ , $\text{cm}^3\text{mol}^{-1}$	$T_g$ (TMA) ( $^\circ\text{C}$ )	$T_g$ (DTA) ( $^\circ\text{C}$ )	$T_{c1}$ ( $^\circ\text{C}$ )	$T_{c2}$ ( $^\circ\text{C}$ )
0.05	5.56	27.58	27.57	-0.01	359	343	400	479
0.1	5.87	26.71	27.38	0.67	348	328	383	457
0.15	6.02	26.63	27.18	0.56	335	313	383	440
0.2	6.14	26.66	26.99	0.33	311	300	360	485

Footnote:  $V_{m,\text{add}} = \sum x_i V_{m,i}$  where  $x_i$  is the molar fraction of an  $i$ th oxide and  $V_{m,i}$  is the molar volume of an  $i$ th oxide. Following values of densities in  $\text{gcm}^{-3}$  were used:  $\rho(\text{PbO}) = 9.64$ ,  $\rho(\text{BaO}) = 5.72$ ,  $\rho(\text{ZnO}) = 5.61$ ,  $\rho(\text{TeO}_2) = 5.67$ . For  $V_{m,i}$  calculation the values of the densities were multiplied by 0.95 since it is reasonable to assume lower density of an oxide in the glassy state in comparison with its crystalline state. The values of CTE were found to be practically independent on the chemical composition:  $\text{CTE} \approx 20.5$   $\text{ppm } ^\circ\text{C}^{-1}$ .

#### 3.1. Structural consideration

The typical Raman spectra for the glasses considered are shown in Fig. 1. It is evident that all the spectra are similar. Two well resolved Raman features at around: 750-765  $\text{cm}^{-1}$  (RF<sub>1</sub>), 660  $\text{cm}^{-1}$  (RF<sub>2</sub>) and two broad RF at around: 450-460  $\text{cm}^{-1}$  (RF<sub>3</sub>) and 310  $\text{cm}^{-1}$  (RF<sub>4</sub>), are

evident. The Raman spectra similarity implies that the substitution of BaO by PbO, for the conserved molar fraction of TeO<sub>2</sub>, does not lead to structural changes visible in the Raman spectra.

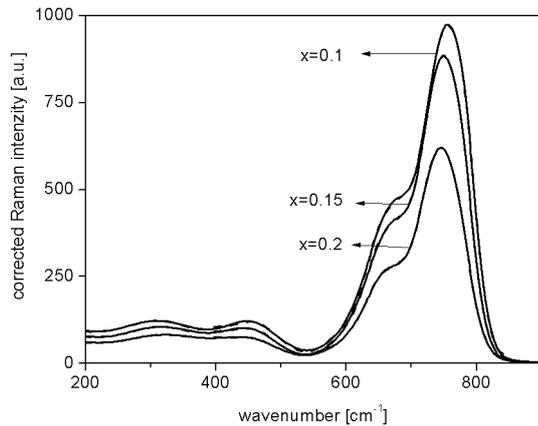
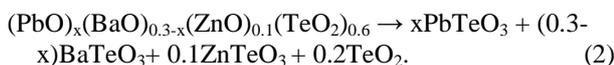


Fig. 1. Corrected Raman scattering spectra of  $(\text{PbO})_x(\text{BaO})_{0.3-x}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$  glasses. The chemical composition is marked on the left hand side ( $x$ ).

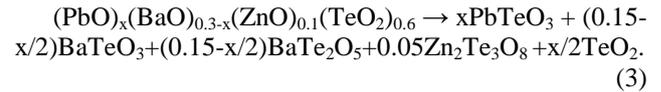
According to the classical assignment of the RF of  $\text{TeO}_2$  based glasses, see e.g. [16], the  $\text{RF}_1$  belongs to the stretching modes of  $\text{Te-O}^-$  or  $\text{Te=O}$  bonds in  $\text{TeO}_{3+1}$  or  $\text{TeO}_3$  trigonal pyramids (tp), the  $\text{RF}_2$  belongs to the antisymmetric vibration of  $\text{Te-O-Te}$  bridges, with non-equivalent  $\text{Te-O}$  bonds, connecting  $\text{TeO}_4$  trigonal bipyramids (tbp). Hence,  $\text{RF}_2$  reflects the density of tbp units as well as their distortion. It should however be noted that both  $\text{RF}_1$  and  $\text{RF}_2$  are broadened which means that  $\text{RF}_1$  could reflect stretching modes of both  $\text{Te-O}_3$  and  $\text{Te-O}_{3+1}$  units and  $\text{RF}_2$  could reflect not only the stretching modes of distorted tp but also the antisymmetric stretching of tbp forming a continuous network.

This type of RF assignment is consistent with the structural studies of the corresponding binary systems. In  $\text{ZnO-TeO}_2$  glasses the network is suggested to be "...an admixture of  $\text{TeO}_4$ ,  $\text{TeO}_{3+1}$  and  $\text{TeO}_3$  units" [17]. In  $\text{BaO-TeO}_2$  the progressive transformation of distorted  $\text{TeO}_{3+1}$  units and the formation of  $\text{TeO}_3$  units is suggested when  $\text{BaO}$  is added to  $\text{TeO}_2$  [18]. In  $\text{PbO-TeO}_2$  system with an increase in the  $\text{PbO}$  content transition from  $\text{TeO}_4$  tpb to  $\text{TeO}_3$  tp proceeds as deduced from the Raman spectra and X-ray absorption spectroscopy [19]. Mirgorodsky et al. [20] have recently advocated a new approach to the structure of certain  $\text{TeO}_2$  based glasses which follow the solid state chemistry grounds. Briefly, for the interaction between  $n$  moles of  $\text{TeO}_2$  and  $m$  moles of  $\text{M}_k\text{O}_l$  modifier,  $M$  ortho-tellurites are formed mixed with neutral  $\text{TeO}_2$  molecules, see rels. 1 and 2 in [20]. Such an approach means that it should be valid:  $E(\text{Te-O}) \geq E(\text{M-O})$ . In our case this condition is partially fulfilled since:  $E(\text{Te-O}) \approx E(\text{Pb-O}) \approx 380$  kJ/mol and  $E(\text{Zn-O}) \approx 160$  kJ/mol [15]. Note, that  $\text{BaO}$  ( $E(\text{BaO}) \approx 560$  kJ/mol, [15]) does not form an anion. The chemical composition of the glasses studied can be expressed as a mixture of ortho-tellurites in the following way:



The idea of the existence of the studied glasses as a mixture of structural units inherent to ortho-tellurite, see eq. 2, is compatible with the results of our Raman spectra since  $\text{RF}_1$  is assigned to the presence of  $\text{TeO}_2$  and  $[\text{TeO}_3]^{2-}$  units,  $\text{RF}_2$  to  $\text{TeO}_2$  [20],  $\text{RF}_3$  to  $\text{Te-O-Te}$ ,  $\text{O-Te-O}$  symmetrical stretching and/or bending vibrations [16] and  $\text{RF}_4$  can be assigned to  $\text{Te-O-Zn}$  bending [9].

The other possibility for expressing the glasses considered as a mixture of the binary compounds of the corresponding systems is shown by eq. (3):



This expression reflects the fact that in  $\text{BaO-TeO}_2$  system there exists the eutectic composition specifically at the molar ratio  $\text{BaTeO}_3/\text{BaTe}_2\text{O}_5 = 1/1$  [21]. In this case the glass-formation would in all probability be easier to realize than in the case of the formation of the exclusive  $\text{BaTeO}_3$  compound having the melting point at around  $1000^\circ\text{C}$  [21]. The Raman spectra are compatible with the Raman activity of the structural units inherent to the compounds in eq. (3) considered in our case as well. The basic structural units of  $\text{Zn}_2\text{Te}_3\text{O}_8$  compound are  $\text{Te}_3\text{O}_8$  groups built up by two  $\text{TeO}_{3+1}$  and one  $\text{TeO}_4$  units [22] reflected by  $\text{RF}_1$  and  $\text{RF}_2$ , respectively. The compound  $\text{BaTe}_2\text{O}_5$  has a distorted orthorhombic structure which consists of infinite corrugated sheets of corner sharing  $\text{TeO}_{3+1}$  s.u. reflected by  $\text{RF}_1$ , see Fig.1. The glasses considered consequently represent, in all probability, the complicated mixture of tellurites with  $\text{TeO}_2$  neutral molecules.

### 3.2. Optical band gap

The typical spectral dependences of the absorption coefficient in the coordinates  $(\text{Kh}\nu)^{1/2}$  versus  $h\nu$  are shown in Fig. 2. The dotted line indicates the  $E_g$  value determination.

$E_g(T)$  dependences for the glasses studied are shown in Fig. 3. In the measured temperature region the  $E_g(T)$  dependence can be approximated by the simple linear relation:  $E_g(T) = E_g(T \rightarrow 0) - \gamma T$  where the coefficient of the temperature dependence of the optical band gap ( $\gamma$ ) is at around  $\gamma \approx 3.3 \times 10^{-4}$  eV $\text{K}^{-1}$  and is comparable to  $\gamma$  values of various other oxide glasses [23].

Certain optical parameters of the glasses studied are summarized in Table 2. It is apparent from Table 2 that the optical band gap decreases with an increase in  $\text{PbO}$  content.

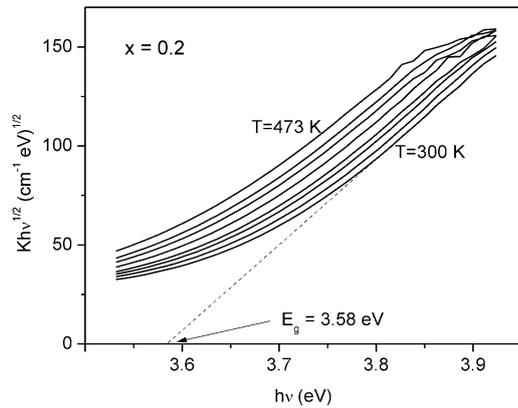


Fig. 2. The typical red shift of the short wavelength absorption edge with temperature (coordinates  $(Kh\nu)^{1/2}$  vs.  $h\nu$ ), here for  $(\text{PbO})_{0.2}(\text{BaO})_{0.1}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$  glass (the sample thickness  $d \cong 3 \mu\text{m}$ ). The temperature increment from the  $T = 300 \text{ K}$  was  $25 \text{ }^\circ\text{C}$ . The dashed line illustrates the optical band gap determination.

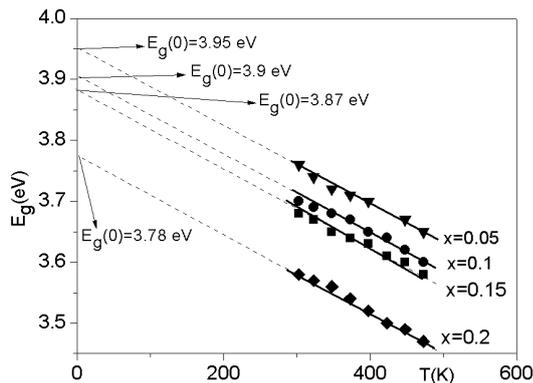


Fig. 3. The temperature dependence of the optical band gap for  $(\text{PbO})_x(\text{BaO})_{0.3-x}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$  glasses. Dashed lines illustrate the linear extrapolation according to relation  $E_{g,\text{non}}(T) = E_{g,\text{non}}(0) - \gamma T$ . The chemical composition is marked on the right hand side.

This seems to be in agreement with the concept of local gap additivity [24] since the substitution of BaO by PbO should lead to the optical band decrease because:  $E_g(\text{BaO}) = 3.9 \text{ eV}$  [25]  $>$   $E_g(\text{PbO}) = 2.7\text{-}2.8 \text{ eV}$  [26]. Also as pointed by Li et al. [27], an increase in the content of Pb in oxide glasses shifts the UV absorption edge into long wavelengths as the optical band decreases due to an increase in polarizability of Pb-O bonds.

Of interest is, however, the observed decrease in the slope ( $B^{1/2}$ ) of the SWAE, see Table 2. Within the Mott-Davis model [13] the slope of SWAE reflects a disorder which measures the width of localized states at the conduction band ( $\Delta E_c = E_c - E_a$ ) or valence band ( $\Delta E_v = E_b - E_v$ ) where  $E_g = E_c - E_b$  or  $E_a - E_v$ , whichever is smaller and  $\Delta E_c = \Delta E_v = \Delta E$  is assumed.

Here  $E_c$  is the bottom of the conduction band,  $E_v$  is the top of the valence band,  $E_b$  is the top of valence band tail,  $E_a$  is the bottom of the conduction band tail.

Table 2. The chemical composition ( $x$ , molar fraction), the optical band gap ( $E_g$ ), the refractive index ( $n$ ), the slope of SWAE ( $B^{1/2}$ ) and the width of localized states ( $\Delta E$ ).

$x$ , PbO	$E_{g,\text{non}}$ (eV)	$n$	$B^{1/2}$ ( $\text{cm}^{-1/2}\text{eV}^{-1/2}$ )	$\Delta E$ (eV)
0.05	3.75	1.9 <sub>5</sub>	$\approx 800$	$\approx 0.09$
0.1	3.71	2.0 <sub>5</sub>	$\approx 700$	$\approx 0.11$
0.15	3.68	2.0 <sub>5</sub>	$\approx 500$	$\approx 0.17$
0.20	3.58	2.1 <sub>5</sub>	$\approx 500$	$\approx 0.20$

Footnote: The values of the refractive index estimated from the optical transmission in the transparent region ( $n = 1/T_0 + [(1/T_0^2) - 1]^{1/2}$ ) where  $T_0$  is the optical transmission in the transparent region.

In this model the slope of SWAE is provided by the relation:  $B = 4\pi\sigma_{\text{min}}/nc\Delta E$ , where  $\sigma_{\text{min}}$  is the minimum metallic conductivity,  $n$  is the refractive index and  $c$  is the light velocity. Assuming  $\sigma_{\text{min}} \approx 300 \Omega^{-1}\text{cm}^{-1}$  [13] we estimated the  $\Delta E$  in the region  $0.09 < \Delta E, \text{ eV} < 0.2$ , hence, the change in the width of localized states  $\Delta(\Delta E) \approx 0.11 \text{ eV}$  is comparable to the changes in the optical band gap  $\Delta E_g = 3.75 - 3.58 = 0.17 \text{ eV}$ . The optical band gap reduction with an increase in  $x$  can consequently be interpreted as a result of an increase in disorder  $x$ . We tentatively assume that the optical transitions responsible for the measured SWAE are from  $E_v$  to  $E_a$ .

#### 4. Conclusion

Based on the results obtained we conclude that the substitution of BaO by PbO in  $(\text{PbO})_x(\text{BaO})_{0.3-x}(\text{ZnO})_{0.1}(\text{TeO}_2)_{0.6}$  glasses does not lead to significant changes in the overall structural arrangement of the glassy network. Independent, however, of whether the classical approach or the approach by Mirgorodsky et al. [20] is used for the explanation of the Raman scattering observed it is certain that the substitution of BaO by PbO leads to a certain increase in the disorder associated in all probability with an increase in the number of structural units forming the network. Within the Mott-Davis model the decrease in the optical band gap in the glasses considered is consequently compatible with an increase in the width of the localized states at the conduction band.

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## References

- [1] R. A. El-Mallawany, Tellurite Glasses Handbook, CRC INC. Boca Raton, 2002.
- [2] T. Sekiya, N. Mochida, A. Ohtsuka and M. Tonokawa, *J. Non-Cryst. Solids* **144**, 128 (1992).
- [3] M. D. Donnell, A. B. Seddon, D. Furniss, V. K. Tikhomirov, C. Rivero, M. Ramme, R. Stegman, G. Stegman, K. Richardson, R. Stolen, M. Couzi, T. Cardinal, *J. Amer. Cer. Soc.* **90**, 1448 (2007).
- [4] C. Riviero, R. Stegeman, K. Richardson, G. Stegeman, G. Turri, M. Bass, P. Thomas, M. Udovic, T. Cardinal, E. Fargin, M. Couzi, H. Jain, A. Miller, *J. Appl. Phys.* **101**, 023526 (2007).
- [5] J. E. Stanworth, *Nature* **169**, 581 (1952).
- [6] S. Suehara, Y. Yamamoto, S. Hishita, T. Aizawa, S. Inoue, A. Nukui, *Phys. Rev. B* **51**, 14919 (1995).
- [7] R. A. Naraynan, J. W. Zwanziger, *J. Non-Cryst. Solids* **316**, 273 (2003).
- [8] A. Kaur, A. Khanna, C. Pesquera, F. Gonzales, V. Sathe, *J. Non-Cryst. Solids* **356**, 864 (2010).
- [9] N. Manakindan, A. Ryasnyanskiy, J. Toulouse, *J. Non-Cryst. Solids* **358**, 957 (2012).
- [10] G. E. Rachkovskaya, G. B. Zakharevich, *Glass and Ceramics* **59**, 123 (2002).
- [11] K. Vosejpkova, private communication.
- [12] K. Kotkova, H. Ticha, L. Tichy, *Optoelectron. Adv. Mater. – Rapid Comm.* **1**, 36 (2007).
- [13] E. A. Davis, N. F. Mott, *Philos. Mag.* **68**, 903 (1970).
- [14] J. I. Pankove, *Optical Processes in Semiconductors*, Plenum, New York, 1974.
- [15] *Handbook of Chemistry and Physics* 49<sup>th</sup> Edition, R. C. West editor, The Chemical Rubber Co., Ohio 1968.
- [16] G. S. Murugan. Y. Ohishi, *J. Appl. Phys.* **96**, 2440 (2004).
- [17] H. A. A. Sidek, S. Rosmawati, Z. A. Talib, M. K. Halimah, W. M. Daud, *Am. J. Appl. Sciences* **6**(8), 947 (2012).
- [18] A. N. Begun, V. Rajendran, *Mater. Lett.* **61**, 2143 (2007).
- [19] M. A. P. Silva, Y. Messadeeq, S. J. L. Riberio, M. Poulain, F. Villain, V. Briois, *J. Phys. Chem. Solids* **62**, 1055 (2001).
- [20] A. Mirgorodsky, M. Coals, M. Smirnov, T. Merlen-Méjean, R. El-Malawany, P. Thomas, *J. Solid St. Chemistry* **190**, 45 (2012).
- [21] R. Mishra, S. Phapale, P. Samui, A. Nagaraj, S. R. Dharwadkar, *J. Phase Equilib. Diffusion* **35**(2), 127 (2014).
- [22] K. Hanke, *Naturwissenschaften* **53**, 273 (1966).
- [23] H. Ticha, M. Kincl, L. Tichy, *Mat. Chem. Phys.* **138**, 633 (2013).
- [24] K. Shimakawa, *J. Non-Cryst. Solids* **43**, 229 (1981).
- [25] T. Ly, D. Chen, M. Huang, *J. Appl. Phys.* **100**, 086103 (2006).
- [26] H. J. Terpstra, R. A. deGroot, C. Haas, *Phys. Rev. B* **52**, 1169 (1995).
- [27] H. Li, M. Nogami, Y. Abe, *J. Mater. Res.* **9**(9), 2319 (1994).

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