Chromium doped (80-x)Sb$_2$O$_3$-20K$_2$O-xPbO glasses: Effects of PbO on the optical properties in Urbach's rule region

P. PETKOVA[a], K. BOUBAKER[b], M.T. SOLTANI[c], P. VASILEV[a], G. ALEXIEVA[d]

[a]*Shumen University "Konstantin Preslavsky", 115 Universitetska street, 9712 Shumen, Bulgaria*
[b]*École Supérieure de Sciences et Techniques de Tunis (ESSTT), Université de Tunis/63 Rue Sidi Jabeur, 5100, Mahdia, Tunisia*
[c]*Dept. of Physics, Faculty of Sciences and Engineering sciences, University "Mohamed Khider", 07000 Biskra, Algeria*
[d]*Dept. of Solid State Physics and Microelectronics, Faculty of Physics, Sofia University "St. Kliment Ohridski", James Boucher 5, 1164 Sofia, Bulgaria*

The optical absorption of Cr doped (80-x)Sb$_2$O$_3$-20K$_2$O-xPbO glasses is measured in the spectral region 2,75-3,35 eV at room temperature. Optical band gap, Urbach energy and other physical parameters for different PbO concentrations are calculated and discussed. An interpretation of the obtained results is given in the frame of the Lattice Compatibility Theory (LCT).

1. Introduction

It is well known that the shape of the fundamental absorption edge in the exponential (Urbach) region can yield information on the disorder effects [1]. When the energy for the incident photon is less than the band gap, the increase in absorption coefficient is followed with an exponential decay of density of states localized into the gap [2] and the absorption edge is known as Urbach edge. The lack of crystalline long-range order in amorphous/glassy materials is associated with a tailing of density of states [2]. In this paper we report our investigations on the optical properties of new antimony glasses, doped with chromium.

Antimony oxide emerges as one major component of heavy metal oxide glasses (HMOG) which comprise a group of glassy materials formed essentially by Sb$_2$O$_3$, Te$_2$O, WO$_3$, PbO or Bi$_2$O$_3$ [3-8]. They have several advantages over conventional silicate, borate or phosphate glasses due to their superior physical properties such as high density, high refractive index, low melting and softening temperatures and high infrared transmission. The phonon energy of Sb$_2$O$_3$ glasses close to 600 cm^{-1} [5] is much lower compared to glasses containing lighter elements such as silicon, boron or phosphorus. Thus, antimony glasses are more transparent in the infrared light than borate, phosphate or silicate conventional glasses and also more than its corresponding HMOG glasses. In view of these qualities, the glasses were considered as the best materials for optical components such as IR domes, optical filters, modulators, memories and laser windows. Further, these glasses were also considered as very good materials for hosting lasing ions like transition metals or rare-earth ions, since these glasses provide a low phonon energy environment to minimize non-radiative losses [9]. In view of these qualities, chromium doped glasses in the (80-x)Sb$_2$O$_3$-20K$_2$O-xPbO system (x = 10-30 (mol %) are interesting object that gives the possibility to explore their structure by using chromium (like a coloring agent with broad radial distribution of outer d-electron orbital function), as well as because of their high sensitive response to changes in surrounding actions. In this paper, the investigation was examined from the absorption spectra in visible range by analyzing the different absorption bands due to chromium ions. Chromium in a silicate glass normally distributes into Cr^{3+} and Cr^{6+} and a green colour is produced by Cr^{3+} linked in octahedral sites with three absorption bands located in 635nm (1,95 eV), 650 nm (1,91 eV) and 675 nm (1,84 eV) [6]. It is also reported that Cr^{4+} can exist in some glasses like alumina-silicate, alkaline-earth aluminate or gallate glasses with large modifier content [10].

The aim of our work is to calculate the optical band gap, Urbach's energy, and the change of other spectral parameters which characterize the two variants of the Urbach's rule.

2. Experimental

Reagent grade chemicals Sb$_2$O$_3$, K$_2$CO$_3$, PbO and Cr$_2$O$_3$ (99.6%) were used as starting materials to prepare glass samples in the ternary glassy composition: (80-x)Sb$_2$O$_3$-20K$_2$O-xPbO, were x = 0, 10, 20 and 30 (mol %).

These glasses have been synthesized and processed using classical routes. They were prepared in open silica glass crucibles with 10 mm in diameter. Powder mixtures of the components (5g) were flame heated until a clear and homogenous liquid is obtained and then the melt were cast onto a brass plate. The samples were annealed at 250°C for 6 hours in order to minimize mechanical stress resulting from thermal gradients upon cooling. Finally, they were cut and polished.

The experimental set up for measurement of the absorption coefficient in the Urbach's rule region has the following parts: a halogen lamp with stabilized rectifier 3H-7, a monochromator SPM-2, a system of quartz lenses, a polarizer, a glass holder with a sample and a detector Hamamatsu S2281-01. The experimental data are measured in the spectral region 2,75-3,35 (eV). The spectral dependence α (E) of all test samples at the temperature T = 300 K is given in Fig. 1.
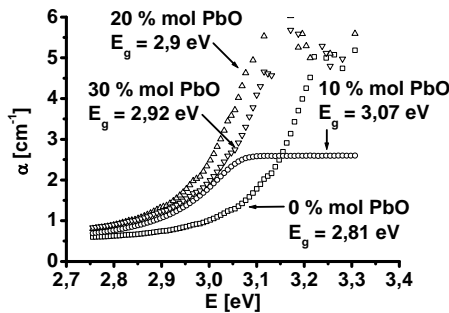

Fig. 1. The absorption coefficient α(E) for undoped and Cr doped glasses in the spectral region 2,75-3,35 eV.

3.Results and discussion

3.1. Theoretical background and results

It is well known that the Urbach's tail is directly related to the occurrence of structural disorder in glass systems [11]. Here we are going to discusse the "crystalline" and "glassy" variants of Urbach's rule in the case of Cr doped $(80-x)Sb_2O_3-20K_2O-xPbO$ glasses.

It can be expected that Urbach's rule is fulfilled when the absorption coefficient near the fundamental edge exhibits exponential dependence $\ln\alpha = A+B*(\hbar\omega/T)$, where A and B are constants, T is the temperature. The constant B is expressed by the dependence $B = \sigma(T)/k$, where $\sigma(T)$ is the parameter characterizing the slope of the absorption edge, k is the Boltzmann constant.

In the "crystalline" variant we determined the logarithmic slope of the absorption coefficient and after that we calculated the constant α_0 (Eq. 1) and the parameter σ (Eq. 2) [11]. The constant α_0 is expressed by:

$$\alpha(h\nu,T)=\alpha_0 \exp\left(\frac{h\nu-E_g(T)}{E_0(T,X)}\right). \tag{1}$$

In this equation, E_g (T) is the width of the band gap, X is the geometric parameter of the material characterizing

the component of the static disorder in Urbach's rule [11]. σ is expressed by the ratio:

$$\sigma(T)=\sigma_0 \frac{2kT}{\eta\omega}\tanh\left(\frac{\eta\omega}{2kT}\right). \tag{2}$$

The position of the absorption edge and hence the optical band gap were found to depend on the glass composition. The absorption edge of our samples shifts to higher energy values in comparison with 0 % mol PbO (Fig. 2).
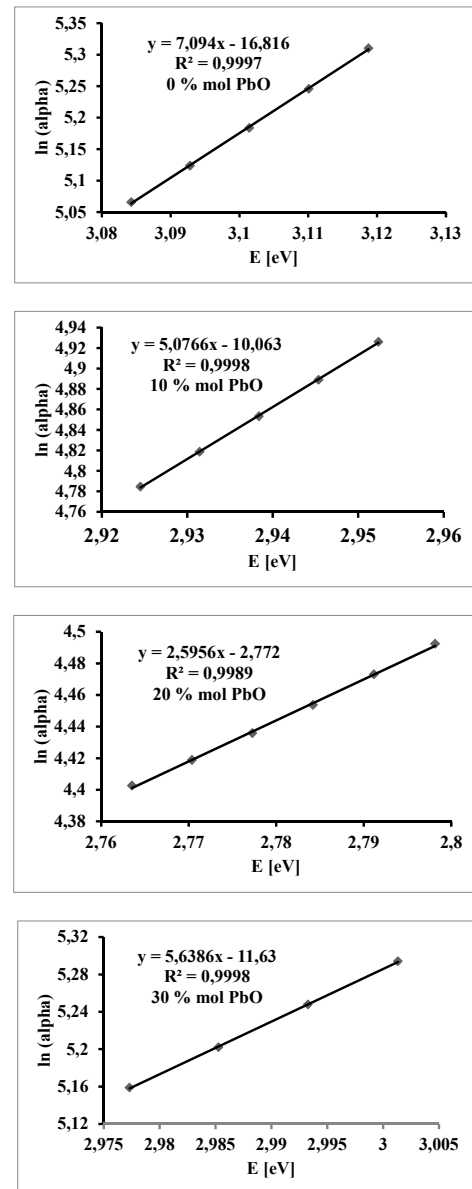

Fig. 2. Calculated data for lnα (E) for undoped and Cr doped glasses in the spectral region 2,765-3,120 eV.

The calculated values of α_0 and σ for our samples are presented in Table 1.

Table 1. Parameters of modified Urbach's rule in undoped and Cr doped $(80-x)Sb_2O_3$-$20K_2O$-$xPbO$ glasses at T = 300 K.

PbO content (% mol)	α_0	σ	E_0 [meV]	$K\langle u^2 \rangle_T$ [meV]
0	0.6341	0.1738	141	149
10	1.4634	0.1312	197	197
20	0.7446	0.0671	389	386
30	0.7761	0.1458	182	178

The constant α_0 increases in the case of Cr doped glasses with content of 10, 20 and 30 % mol PbO and it decreases for the sample with 0 % mol PbO. The values of parameter σ decrease when PbO was added to the composition of the Cr doped glasses. The parameter σ and $K\langle u^2 \rangle_T$ depend on the temperature and it could be observed that $K\langle u^2 \rangle_T$ follows the change of E_0 in Cr doped samples.

As it is known, the "glassy" Urbach's rule describes the temperature independent slope of the absorption coefficient. The parameter $E_0 = 1/(\partial \ln \alpha / \partial h\nu)$ is known as Urbach's energy or Urbach's slope [7, 11]. The values of E_0 at T = 300 K for all examined PbO concentrations are presented in Table 1. Respectively, the concentration behavior of E_0 is presented on Fig. 3.
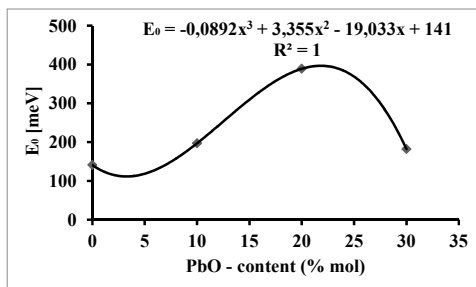

Fig. 3. Urbach's energy E_0 as a function of PbO (% mol). (Solid line fitting)

So, we can compare the contribution of the dynamic and static atomic disorders to the total structural disorder [1, 12]. The function $E_0(T, X) = K(\langle u^2 \rangle_T + \langle u^2 \rangle_X)$ includes the influence of the thermal and frozen phonons.

The contribution of the thermal phonons is expressed by the equation $K\langle u^2 \rangle_T = kT/\sigma(T)$ and it follows the behavior of the constant α_0 (Table 1). The energy of the frozen phonons can be estimated only from the slope of the tails of the spectral dependences in glasses, i.e. the value of the parameter $E_0 = K\langle u^2 \rangle_X = const$. In our glasses, Urbach's energy is on the order of $E_0 = 141 \div 389$ meV.

The form of the absorption edge for the transition of the electrons from the valence band to the free chromium states is studied by Green's functions [13]. If the valence or the impurity state electrons interact with the monoenergetic phonons the absorption edge is of an exponential form as it should be in our case. We assume that the high value of E_0 for the doped sample with 20 % mol PbO is associated with blocking of some LO or TO phonons. It can be expected that a structural change in the glassy matrix of antimony glasses occurs with changing the rate of the lead's ions. PbO, like MoO_3, is known to exhibit some glass forming ability [14]. It is accepted that the structure of the antimony glasses is based on SbO_3 trigonal pyramids sharing corners [15]. We assume also that PbO is able to induce tail states by its deformation potential, by Coulomb interactions [16] and by forming an impurity band [17]. In this case, the value of E_0 is correlated with the impurity concentrations of the sample [18, 19]. The parameter $E_0(x)$ that characterizes the forbidden band can be presented as $E_0(x) = a + bx + cx^2$ (a, b and c are real parameters) [20].

In our case the equation $E_0 = -0.0892x^3 + 3.355x^2 - 19.033x + 141$ describes the dependence of E_0 as a function of PbO concentration. We found that E_0 increases as the concentration of PbO doping reaches to 20 % mol. (Fig. 3).

3.2. Lattice compatibility theory application

The Lattice Compatibility Theory (LCT) is based on the interaction of doping-element lattice behavior versus host edifice, as shown in some recent studies [21-25]. Preludes to this theory have been established by Petkova *et al*. [21] and Boubaker *et al*. [22-24] in context of analysing the stability of some doped compounds. An original formulation of the Lattice Compatibility Theory [24] has been given as the following:

"The stability of doping agents inside host structures is favorized by geometrical compatibility, expressed in terms of matching patterns between doping agent intrinsic lattice and those of the host".

In this study (Cr doped $(80-x)Sb_2O_3$-$20K_2O$-$xPbO$), the nature of the highest occupied bands in Cr intrinsic lattice along with bonds configuration parameters have been demonstrated to be determinant. In this context, fundamental geometrical observations concerning the structure of Chromium oxide intrinsic lattice along with that the host matrix $(80-x)Sb_2O_3$-$20K_2O$-$xPbO$ (Fig. 4), could be interpreted here in terms of conventional lattice-linked parameters (bond spatial extent, lattice parameters, angles, etc.).
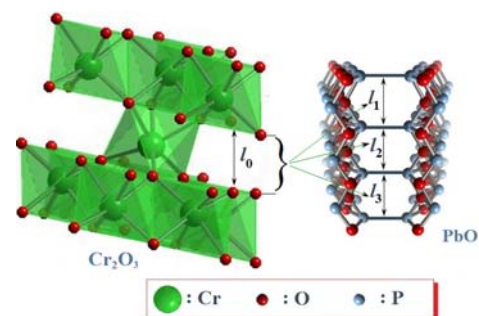

Fig. 4. Chromium oxide-PbO duality scheme in the framework of the Lattice Compatibility Theory LCT

The stability that results from placing Cr ion in the crystal field generated by a set of surrounding electrophil (electron-attracting) group, makes chromium d-orbitals split in a ligand field, in the manner that, if there are any electrons occupying these orbitals, then the metal ion is more stable in the surrounding field. Nevertheless, in terms of LCT, this stability is likely to be forbidden due to the obvious lengths incompatibility (l_0 versus l_1, l_2 and l_3). Such an irregularity has been recorded by Raghavaiah *et al.* [26] and Srinivasarao *et al.* [27].

The second scheme (Fig. 5) gives evidence to the preferential chromium ions incorporation within Sb_2O_3 lattice.
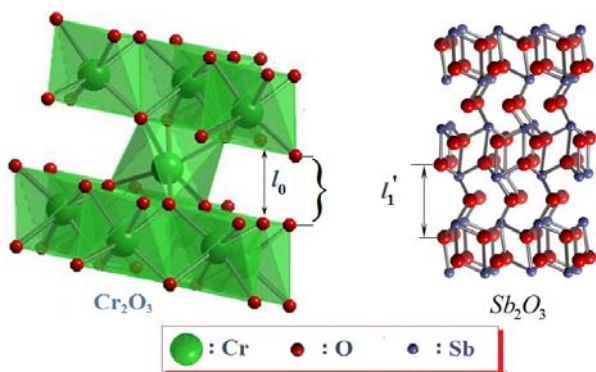

Fig. 5. Chromium oxide-Sb_2O_3 duality scheme in the framework of the Lattice Compatibility Theory LCT

This pattern confirms that Cr^{3+} and Cr^{4+} ions substitute Sb^{3+} in octahedral position within $(80-x)Sb_2O_3$-$20K_2O$-$xPbO$ lattice, as already indicated by Pekova *et al.* [28]. Hence, the Lattice Compatibility Theory *LCT* gives an explanation to the recorded behavior of chromium ion in these glasses.

4. Conclusions

Cr-doped glasses in $(80–x)Sb_2O_3–20K_2O–xPbO$ have been synthesized and optical characterization has been performed. Parameters of modified Urbach's rule at T = 300 K in undoped and Cr doped glasses for different PbO concentrations are calculated. The values of lnα (E) are higher for the glasses with 0 and 30 % mol PbO. The energy gap is highest for the sample with 10 % mol PbO. The thermal phonons are most in the glass with 20 % mol PbO at room temperature. Obviously, this type of glasses deserves further studies in order to elucidate the found interesting peculiarities in the interplay of effects coming from their doping and oxide components. The LCT was applied to discuss the local environment of chromium ions and to confirm that Cr^{3+} and Cr^{4+} ions substitute Sb^{3+} ions in the host lattice.

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*Corresponding author: gerry@phys.uni-sofia.bg