

Urbach's Rule in Undoped and Co Doped (80-x)Sb₂O₃-20Na₂O-xWO₃ Glasses

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We have analyzed the Co influence on the absorption spectra of (80-x)Sb₂O₃-20Na₂O-xWO₃ glasses in the Urbach rule region at room temperature. We present the comparison between Co and WO₃ manifestation in the spectral region 2.64–3.14 eV. The spectral characteristics of "crystalline" and "glassy" Urbach's rule are also calculated.

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1. Introduction

The UV-V spectroscopy of insulating glasses is very helpful in the study of materials. From the amorphous to the crystalline materials, the fine slope absorption edge is becoming very sharp. Several attempts have been carried out to present a common mechanism for the formation of the absorption edge of the crystalline and the amorphous solids, governed by the so-called Urbach rule [1], but there still is no universal interpretation of the nature of this rule. The values of Urbach's spectral parameters depend on the energetic position and the shape of the absorption edge. These values are changing under the influence of doping with impurities, irradiation, increase or decrease of the temperature, the mechanical action, etc. These effects lead to a considerably distorted absorption edge. The expectations for a distorted absorption edge are not feasible in many glasses.

In this paper, we investigate new antimony glasses, doped with cobalt. The antimony oxide as a part of the heavy metal oxide (HMO) glasses is attractive to researchers in recent years. These glasses have low energy of phonons, high refractive indexes and also have extensive IR transmission, which makes Sb₂O₃ glasses conducive to study them in IR region [1–3]. Therefore, crystals, glasses and glass ceramics, containing cobalt ions, are considered as useful for nonlinear optical absorbers, needed for passive modulations of a laser beam and for Q-switching devices [4, 5]; this is due to the fact that they exhibit strong luminescence in the visible and the near-infrared regions (NIR).

In glasses, cobalt ions exist in two stable ionic states as Co²⁺ and Co³⁺. Co²⁺ ions create colour centres (blue or pink or red) with absorption bands in the visible and NIR regions. The cobalt doped antimony glasses, studied in this paper, were synthesized in silicate crucibles. 0.05 mol.% of Co₃O₄ was added to the glass batch in the combination Sb₂O₃-WO₃-Na₂O. The glasses are synthe-

sized after mixing and melting of the starting materials at the room temperature.

Cobalt was used as a structural probe [5]. It was observed that the blue intense colour of the glass, containing 10 mol.% of WO₃, turns to clear blue and finally to green colour when the amount of WO₃ increases from 20 to 40 (mol.%). The blue colour of the glasses is indicative of the presence of the cobalt Co²⁺ in tetrahedral environment; however the change of the intensive blue colour to green for more WO₃ content is indicative for a structural change from the tetrahedral sites to the octahedral environment.

Therefore, the reason for our investigations is connected with the verification of the exponential form of the absorption edge in the undoped and Co doped (80-x)Sb₂O₃-20Na₂O-xWO₃ glasses. The aim of this work is focused on the calculation of the optical parameters of doped and undoped glasses. They concern: the optical band gap, Urbach's energy, and the change of the spectral parameters which characterize the two variants of the Urbach rule.

2. Experimental details

The experimental setup for measurement of the absorption coefficient in the Urbach 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 investigated glasses are of two series: undoped (80-x)Sb₂O₃-20Na₂O-xWO₃ and doped with 0.05 mol.% Co₃O₄. The value of x changes from 10 mol.% WO₃ to 40 mol.% WO₃. The thickness of the glasses varies between 2.15 mm and 2.75 mm. The spectral dependence $\ln \alpha(E)$ of all the test samples at the temperature $T = 300$ K is given in Figs. 1 and 2. The experimental data are measured in the spectral region 2.64–3.14 eV.

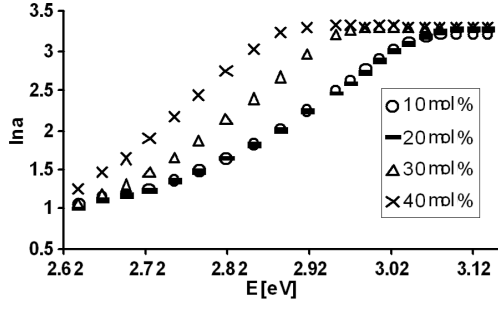


Fig. 1. The experimental data of $\ln\alpha(E)$ for undoped glasses in the spectral region 2.64–3.14 eV.

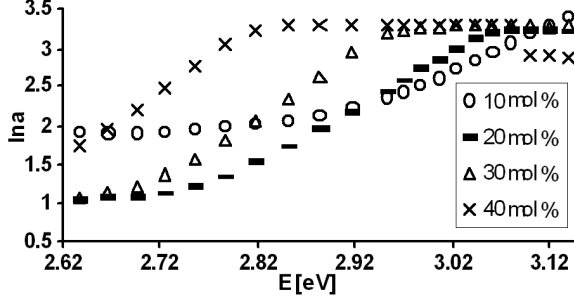


Fig. 2. The experimental data of $\ln\alpha(E)$ for Co doped glasses in the spectral region 2.64–3.14 eV.

3. Results and discussion

It is well known that the Urbach tail is directly related to the occurrence of structural disorder in the glass system [6]. We have discussed the “crystalline” and “glassy” variants of Urbach’s rule in the case of undoped and Co doped $(80-x)\text{Sb}_2\text{O}_3-20\text{Na}_2\text{O}-x\text{WO}_3$ glasses. It can be expected that Urbach’s rule is fulfilled when the absorption coefficient near the fundamental edge exhibits exponential dependence. In the “crystalline” variant, we have determined the logarithmic slope of the absorption coefficient and after that we have calculated the constant α_0 (Eq. (1)) and the parameter σ (Eq. (2)) [6]. The constant α_0 is expressed by the following formula:

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

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 [7]. σ is expressed by the ratio

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

The absorption edge of our samples shifts to the small energy values with increasing concentration of WO_3 (Figs. 1 and 2). The values of α_0 and σ for our samples are presented in Tables I and II. The constant α_0 increases in the case of Co doped glasses with content of 10

and 40 mol.% WO_3 and it decreases for the doped samples with 20 and 30 mol.% WO_3 . Parameter values σ exhibit inverse relationship to that which is associated with α_0 in the Co doped glasses. The parameter σ and $K\langle u^2 \rangle_T$ depend on the temperature and we observe that $K\langle u^2 \rangle_T$ is a constant for Co doped glasses with 30 and 40 mol.% WO_3 .

TABLE I

Parameters of modified Urbach’s rule in undoped $(80-x)\text{Sb}_2\text{O}_3-20\text{Na}_2\text{O}-x\text{WO}_3$ glasses at $T = 300$ K.

WO_3 content [mol.%]	α_0	σ	E_0 [meV]	$K\langle u^2 \rangle_T$ [meV]
10	6×10^{-9}	0.62×10^{-3}	151	0.016
20	2×10^{-8}	0.59×10^{-3}	138	0.015
30	1×10^{-9}	0.7×10^{-3}	145	0.018
40	1×10^{-10}	0.78×10^{-3}	154	0.02

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 [6]. We can see the values of E_0 at $T = 300$ K in Tables I and II for all different WO_3 concentrations. This 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 which means that we can compare the contribution of the dynamic and static atomic disorders to the total structural disorder [8].

TABLE II

Parameters of modified Urbach’s rule in Co doped $(80-x)\text{Sb}_2\text{O}_3-20\text{Na}_2\text{O}-x\text{WO}_3$ glasses at $T = 300$ K.

WO_3 content [mol.%]	α_0	σ	E_0 [meV]	$K\langle u^2 \rangle_T$ [meV]
10	4×10^{-7}	0.5×10^{-3}	126	0.013
20	2×10^{-9}	0.65×10^{-3}	135	0.017
30	3×10^{-10}	0.74×10^{-3}	148	0.019
40	1×10^{-9}	0.75×10^{-3}	150	0.019

The contribution of the thermal phonons is expressed by the equation $K\langle u^2 \rangle_T = kT/\sigma(T)$. The thermal phonons follow the behavior of the constant α_0 (Tables I and II). 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 $E_0 = K\langle u^2 \rangle_X = \text{const}$. In our investigated glasses, Urbach’s energy is of the order of $E_0 = 126 \div 154$ meV. This Urbach’s slope is shifted to the lower energies for the pure and Co doped glasses with the increase of the WO_3 concentration. The form of the absorption edge for the transition of the electrons from the valence band to the free impurity states is studied by Green’s functions [9]. For this case the absorption edge is of an exponential form, if the valence or the impurity state electrons interact with the monoenergetic phonons. The cobalt state electrons do not interact with the monoenergetic phonons, because of the deviations of the exponential form of the absorption edge. We observe

this situation in all our doped samples. We assume that the high value of E_0 for the doped sample with 10 mol.% WO_3 is associated with blocking of some longitudinal optical (LO) or transversal optical (TO) phonons. It can be expected that a structural change in the glassy matrix of antimony glasses occurs with increasing the rate of the tungsten's ions.

WO_3 , like MoO_3 , is known to exhibit some glass forming ability [10]. The structure of the corresponding glasses is based on $[\text{MO}_4]$ tetrahedral and also on $[\text{MO}_6]$ octahedral in the trioxide-rich composition range [11]. It is still believed that the structure of the antimony glasses is based on SbO_3 trigonal pyramids sharing corners [12]. For the low concentrations of WO_3 , the replacement of Sb_2O_3 by WO_3 induces the formation of $[\text{WO}_4]$ tetrahedral. This means that we have creation of non-bridging oxygen and hence. This situation will shift the energy of the optical band gap to low values. For more WO_3 added, octahedral $[\text{WO}_6]$ took place in the glass and the number of octahedral environment increases in the expense of the tetrahedral $[\text{WO}_4]$, this may explain the change of the blue colour to the green in Co doped glasses.

The shift of UV cut-off to the small energies is indicative for the presence of more tungsten in the upper oxidation state (W^{6+}). Consequently, the resulting occupied and unoccupied molecular orbitals of this network will exhibit a smaller energy gap when the network is predominantly composed of W–O bonds, which causes a creation of a large number of donor centres. As a result, the impurity band becomes more extended into the main band gap [13]. We assume also that WO_3 is possibly to induce the tail states by the deformation potential, by the Coulomb interaction, and by the forming an impurity band [14]. In this case, the value of E_0 is correlated with the impurity concentrations of the sample [14, 15]. Sometimes the parameter $E_0(x)$ that characterizes the forbidden band may be presented as $E_0(x) = a + bx + cx^2$ (a , b , and c are real parameters) [16].

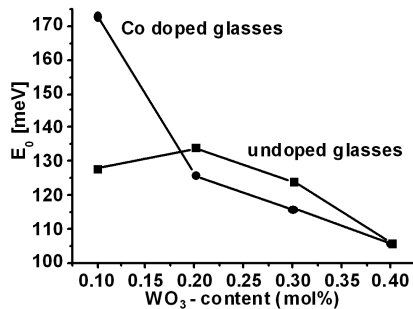


Fig. 3. Urbach's energy E_0 as a function of WO_3 (mol.%). The solid line is a guide for the eye.

The equation $E_0(x) = 0.0113x^3 + 0.0158x^2 - 0.0025x - 0.1292$ describes the dependence of E_0 as a function of WO_3 concentration (Fig. 3). It is found that E_0 decreases

as the concentration of WO_3 doping increases from 20 to 40 mol.%. Therefore, we can say (see Fig. 3) that the different concentrations of WO_3 do not reduce the Co concentration.

4. Conclusions

The calculations of the optical parameters of Co doped and undoped glasses in $\text{Sb}_2\text{O}_3\text{--}\text{WO}_3\text{--}\text{Na}_2\text{O}$ have been carried out. The change of the colour of doped glasses from blue to green colour has been attributed to the structural role of WO_3 in the glass. It is expected that the tetragonal $[\text{WO}_4]$ will exist in the glass giving the blue intense colour of Co doped glasses. For more WO_3 content, the number of the octahedrals $[\text{WO}_6]$ may increase in expense of $[\text{WO}_4]$ to give green colour of the glass. As a result, the parameter σ and the constant α_0 change in the opposite directions in Co doped glasses. The change of $K\langle u^2 \rangle_T$ is such as that of the constant α_0 in doped samples. The increase of content of WO_3 in the glasses does not reduce the cobalt concentration. The Co state electrons do not interact with the monoenergetic phonons in the case of doped glass with content of 10 mol.% WO_3 .

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