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Infrared Spectroscopy of Undoped and Cu-doped (80-x)Sb_2O_3-20Li_2O-xMoO_3 Glasses

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Abstract. In this work, the absorption spectra of the undoped and doped with 0.1% and 0.2% CuO_2 glasses with the composition (80-x)Sb_2O_3-20Li_2O-xMoO_3 are measured in the spectral region 1300-1800 nm. The optical structure of Cu^{2+} is investigated and the energies of the electron transitions in this metal cation are determined. The spin-orbit interaction, Lattice Compatibility Theory (LCT) analyses and the influence of molybdenum are also discussed.

Keywords: doped glasses, absorption infrared spectra, spin-orbit interaction, Lattice Compatibility Theory
PACS: 42.70.Ce, 78.20.Ci, 78.30.Ly

INTRODUCTION

Antimony oxide glasses are attractive, with their low phonon energy and high refractive indices. Sb_2O_3 glasses emerge as a major family of heavy metal oxide (HMO) glasses [1–4] and they have potential applications in nonlinear optical devices such as ultra-fast optical switches, power limiters and broad band optical amplifiers. The glasses and glass ceramics containing cupreous ions are considered to be useful for nonlinear optical absorbers needed for passive modulations of laser beam and for Q-switching devices [5–6]. In glasses, cupreous ions exist in two stable ionic states viz., Cu^{2+} and Cu^{+}. Copper can be an indicator of coordination sites available in a solvent. It gives a bluish green color due to the presence of Cu^{2+} ions in octahedral coordination and does not give any color if copper is in a monovalent oxidation state. Our work was designed to investigate the effect of copper of the changing glass composition on the optical absorption.

EXPERIMENTAL

These glasses were synthesized by conventional method in the ternary system (80-x)Sb_2O_3-20Li_2O-xMoO_3 doped with 0.1 and 0.2 (mol. %) of Cu_2O. Starting materials

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used for the preparation of glasses are commercial products: Sb_2O_3 (Acros 99%), MoO_3 (Aldrich chemical company Inc 99%), Li_2CO_3 (Aldrich > 99.95%) and Cu_2O (Acros 99%).

The experimental set up for measurement of the absorption coefficient in the visible and near IR region consists of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, Glan-Taylor prism which is used as a polarizer, sample holder, and a Hamamatsu S2281-01 detector.

RESULTS AND DISCUSSION

ABSORPTION PATTERNS

The absorption coefficient of the investigated samples has been measured to be between 1300 nm and 1800 nm (Fig. 1, 2, 3 and 4). The absorption coefficient is calculated using the formula:

$$\alpha = (1/d)\ln(I_0/I) \qquad (1)$$

where I_0 is the intensity of the incident light, I is the intensity of the passing light and d is the sample thickness.

A broad absorption band in the visible spectral region was observed for the samples. The first maximum in this band is observed around 1500 nm and the second one is situated around 1725 nm. These maxima can be identified as the d-d transition band due to Cu^{2+} ions. The d-d transitions in Cu^{2+} ions can be described in terms of the ligand field theory. In a regular octahedral field, the $3d^9$ configuration would result in a degenerate ground state (^2E_g). In glasses it is assumed that due to disordered vitreous state which leads to splitting of the energy levels. It is observed that elongated structures are usually more energetically favoured than the compressed ones. For Cu^{2+} in elongated octahedral symmetry more than one structure will be observed. Hence in the present investigation the observed asymmetric band around 6667 cm^{-1} is due to the overlap of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions (Fig. 5). We attribute the observed maximum at 5797 cm^{-1} to the $^2B_{1g} \rightarrow {}^2E_g$ transition in the tetragonal symmetry (Fig. 5). We assume that non-paired electron is situated on the degenerated energetic levels x^2-y^2 and $3z^2$-r^2. These two orbitals contain three electrons and the general stabilization is observed with a decrease in the symmetry. The result is that two electrons traverse on the forming a low energy orbital. This orbital is σ-orbital of the ligands which are connected with the atom of metal [7, 8]. When the octahedron is elongated the following vibration realizes: the fourth ligands in the plane XY approach to the Cu^{2+}cation and the other two ligands which are situated in the plane perpendicular to XY move away from this cation along the z axis. Thus, the two directions of vibration have energetic un-equivalency and the reason is in the asymmetric replenishment of the two degenerated orbitals with the symmetry e_g. One electron is situated on the orbital dx^2-y^2 and two electrons are situated on the orbital dz^2-r^2. The fourth ligands approach to the cation Cu^{2+} in the plane XY and this leads to stabilization of the complex at lower symmetry.

The energy levels of the atomic electrons are affected by the interaction between the electron spin magnetic moment *s* and the orbital angular momentum *l*. In the relativistic approximation the operator of the interaction energy between *s* and *l*, being obtained from the Dirac equation, can be expressed by the following formula [9]:

$$H_{SO} = \xi(r)(l, s) \tag{2}$$

where

$$\xi(r) = (-e/2m^2c^2)(1/r)(\partial V(r)/\partial r) \tag{3}$$

and $V(r)$ is the potential of the nuclei field.

By taking into account the spin-orbit operator as a perturbation, one can calculate the proper corrections for the atomic energy levels. Usually they are defined by the matrix elements of the perturbation, in which the main part is the following value:

$$\xi_{n,l} = \hbar^2 \int \xi(r) R_{n,l}^2(r)dr \tag{4}$$

where $R_{n,l}(r)$ is a radial part of the wave function of the perturbated electron state, $n = 3$ and $l = 2$ (Cu^{2+} ions) are principal and orbital quantum numbers respectively. The term $\xi_{n,l}$ is a so-called spin-orbit interaction constant. While substituting (3) into (4), one can also take into consideration that the Coulomb electrostatic field of the nucleus can be written as:

$$V = Ze/r, \tag{5}$$

where $Z = 29$ (for copper chemical element) is the atomic number, and that average value of the r^{-3} for the so-called hydrogenic wave function can be expressed as [10]:

$$\int r^{-3} R_{n,l}^2(r)dr = (Z^3/a^3n^3)l(l+1)(l+1/2) = 3387.3611*10^{58} \tag{6}$$

where $a = \hbar^2/me = 0.0764*10^{-18}$.
Then, the equation (3) can be re-written in the following way:

$$\xi_{n,l} = Ze^2\hbar^2/2m^2c^2a^3\int r^{-3} R_{n,l}^2(r)dr = 138.6604*10^{-6} \tag{7}$$

When a system has more, than one electron, the total perturbation of the spin-orbit interaction can be expressed by the equation:

$$H_{SO} = \sum \xi(r_i)(l_i, s_i) \tag{8}$$

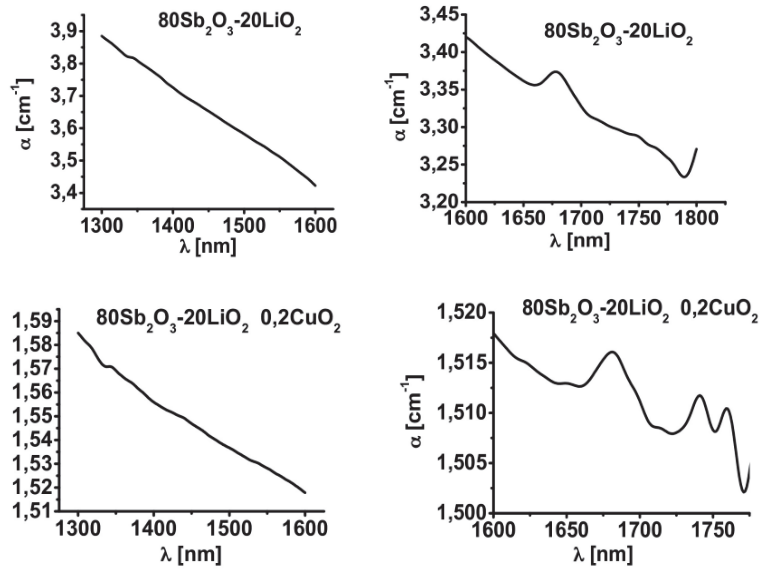

Figure 1. The absorption spectrum of undoped and Cu doped 80Sb$_2$O$_3$-20LiO$_2$ glasses in the spectral region 1300 – 1800 nm.

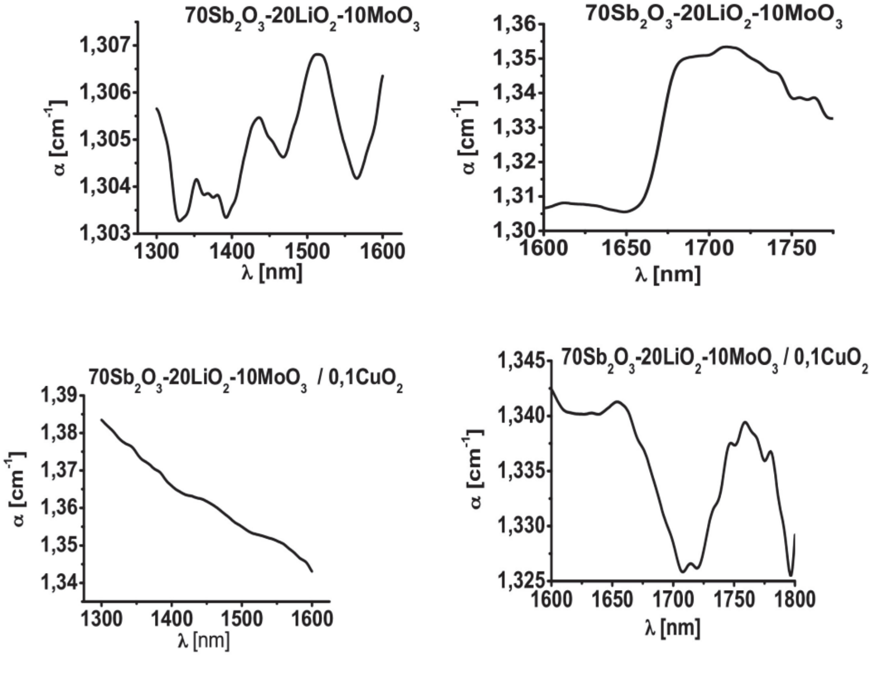

Figure 2. The absorption spectrum of undoped and Cu doped 70Sb$_2$O$_3$-20LiO$_2$-10MoO$_3$ glasses in the spectral region 1300 – 1800 nm.

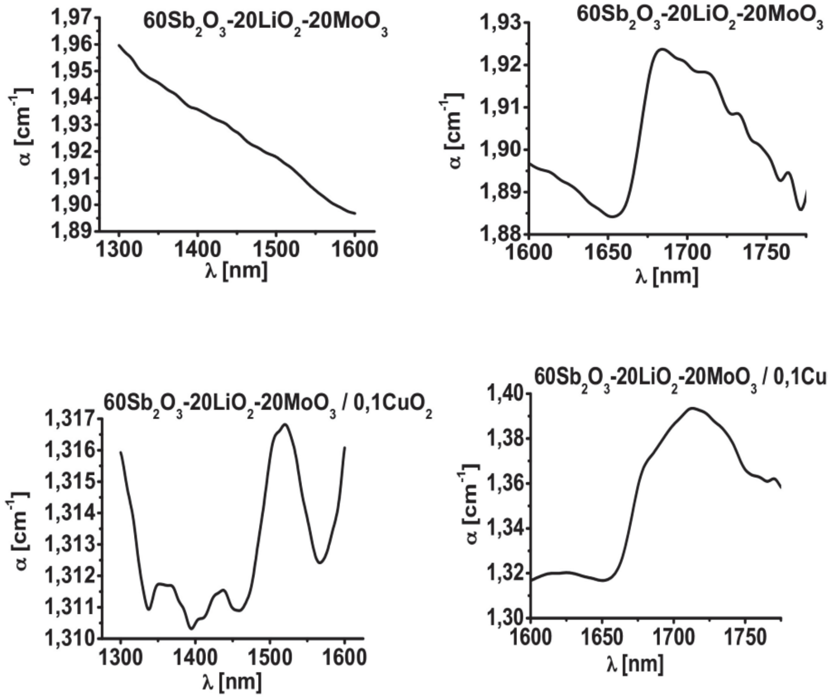

Figure 3. The absorption spectrum of undoped and Cu doped $60Sb_2O_3$-$20LiO_2$-$20MoO_3$ glasses in the spectral region 1300 – 1800 nm.

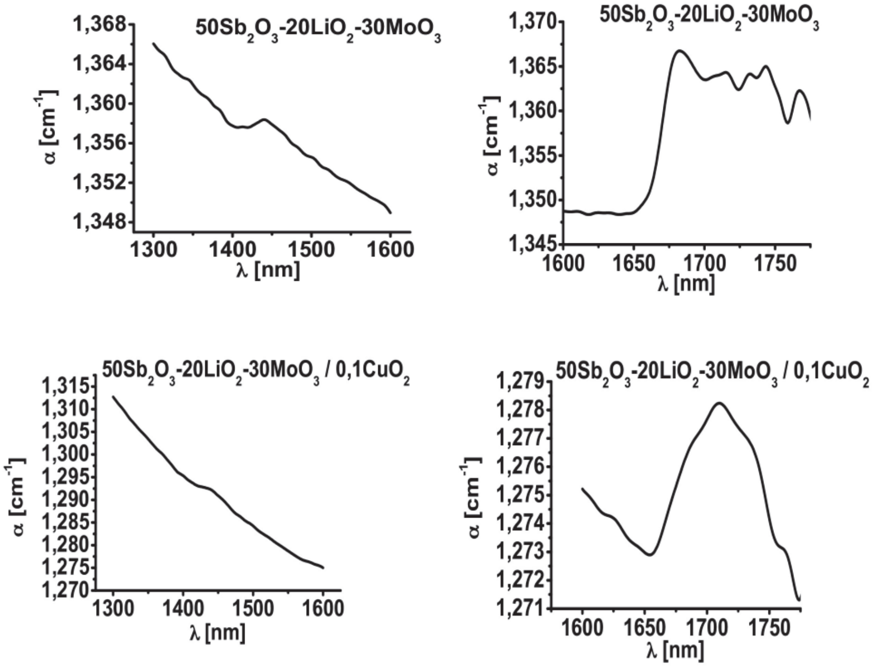

Figure 4. The absorption spectrum of undoped and Cu doped $50Sb_2O_3$-$20LiO_2$-$30MoO_3$ glasses in the spectral region 1300 – 1800 nm.

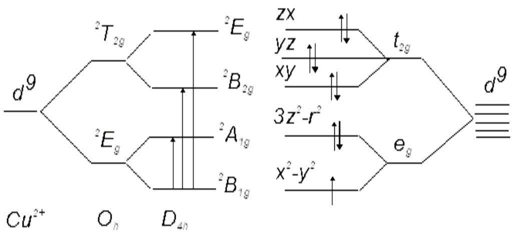

Figure 5. The energetic diagram of the 3d electron transitions in Cu^{2+}.

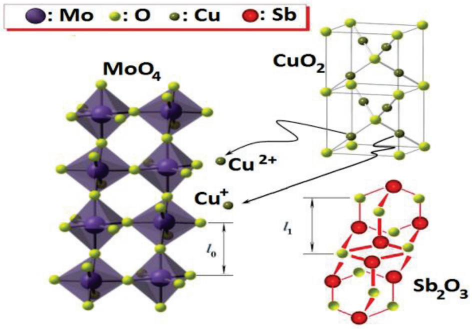

Figure 6. Molybdenum upgraded oxide MoO_4-Sb_2O_3 duality scheme in presence of copper ions in the framework of the Lattice Compatibility Theory LCT.

In case of LS-bound spin-orbital interaction is assumed to be weak, thus, it can be counted as a perturbation of the states with perfect L and S. In this case, it was also shown [9], that the spin-orbit operator can be represented by the formula:

$$H_{SO} = \lambda(LS) = 502 \text{ cm}^{-1} \tag{9}$$

where λ = 828 cm^{-1} (Cu^{2+} ions) is a constant of a spin-orbit interaction, being called spin orbit-parameter and $S = (S_x, S_y, S_z)$ is the spin operator. In the case of Cu^{2+} ions, the spin angular momentum is S= ½, the orbital angular momentum is L = 2 and the total angular momentum is J = 5/2.

The ions of molybdenum inculcate high activity and selectivity in a series of oxidation reactions of practical importance in the glass matrices [11, 12]. A considerable number of interesting studies are available on the environment of molybdenum ion in various inorganic glasses [13−18] Mo−O bond in molybdenum hexavalent oxide is identified as significantly covalent. The Mo ion exists at least in two stable valence states viz., Mo^V and Mo^{VI} in the glass network. Molybdenum ions act both as network formers as well as network modifiers depending upon their concentration and nature of the host network. Most of the studies available on MoO_3 containing glasses are on the understanding of their structure by spectroscopic investigations [19−21] and ionic conductivity studies [22]. Molybdenum trioxide (MO_3) forms glasses [23-30] fairly easily in which Mo is known to exist in Mo^{5+} ($4d^1$) and Mo^{6+} ($4d^0$) states [27, 29-31]. These glasses are known to contain $[MoO_{6/2}]$ or $[OMoO_{5/2}]^-$ groups [32] in the glass network. Due to thermal excitation the Mo^{5+} ($4d^1$) unpaired electron, which is essentially a small polaron [33, 34], hops from a Mo^{5+} site to a Mo^{6+} site. So from the polaronic viewpoint, the electron delivered by the impurity atom at the Mo^{6+} site converts this into a lower valence state Mo^{5+}, and at the next stage, the trapped electron at this Mo^{5+} site is transferred to the neighboring new Mo^{6+} site by absorbing a photon energy. Our assumption is connected with the following statement. The creations of Mo–O–Sb mixed bonds, which are not typical bridging, ones do not deteriorate the glass formation in a limited concentration range. The increase of the number of Mo–O–Mo mixed bonds leads to an increase in the number of small mobile units in the melt (isolated MoO_4 tetrahedra). The accumulation of a critical number of MoO_4 tetrahedra makes the stability of amorphous network questionable. This defines the lower glass formation boundary. The structure of (Sb_2O_3–MoO_3) glasses has been proposed to be similar to those of crystalline phases of the Sb_2O_3–MoO_3 system in proportions that depend on the glass composition. Because of the presence of both of the formers in the vitreous range studied here, –Mo–O– and –Sb=O bonds are transformed into –O–Mo–O– and –Sb–O–Mo– bridging bonds when Mo/Sb ratio increases. Our future experimental and theoretical investigations are seeking to prove this statement.

LATTICE COMPATIBILITY THEORY (LCT) ANALYSES

The Lattice Compatibility Theory is an updated analyses scheme which starts from the interaction of doping-element lattice behavior versus host edifice, as mentioned in some recent studies [35-38]. Preludes to this theory have been established by Petkova *et al*. [35] and Boubaker *et al*. [36-38] in the context of analysing stability of some doped compounds. An original formulation of the Lattice Compatibility Theory [35] has been established as 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 (Cu doped (80-x) Sb_2O_3-20Li_2O-xMoO_3), the nature of the ionic nature (Cu^{2+}/ Cu^{+}) and highest occupied bands in Cu intrinsic lattice along with bonds configuration parameters have been demonstrated to be determinant. In this context, fundamental geometrical observations concerning the structure of intrinsic Copper intrinsic oxide lattice along with that the host matrix (80-x) Sb_2O_3-20Li_2O-xMoO_3 (Fig. 6), were interpreted in terms of conventional lattice-linked parameters (bond spatial extent, atomic/ionic radii, lattice parameters, angles, etc.). The stability that results from placing Cu^{2+} ion in the Sb_2O_3–MoO_3 crystal field generated by a set of surrounding electrophil (electron-attracting) groups makes MoO_3 crystal split into MoO_4, the manner that, if there are any electrons occupying these orbitals, Cu^{2+} ion is more stable in the surrounding field. The Lattice Compatibility Theory *LCT* gives hence an explanation to the recorded behavior of Cu^{2+} ion-induced Molybdenum upgraded oxide MoO_4 within Sb_2O_3 lattice in this glass (§3.1).

CONCLUSIONS

The spin-orbit Hamiltonian is calculated for the Cu doped oxide glasses. The comparison between absorption structures of un-doped and Cu doped glasses shows:

- Antimony gives a very little structure around 1675 nm and Cu^{2+} ions increase it (Fig. 1).
- The Lattice Compatibility Theory *LCT* gives an explanation to the recorded behavior of Cu^{2+} ion-induced Molybdenum upgraded oxide MO_4 within the existent Sb_2O_3 lattice.
- The molybdenum ions give two complicated structures: first of them around 1500 nm and the second in the spectral region from 1650 nm to 1800 nm.

The next step of our investigation is the calculation of this Hamiltonian in the magnetic field.

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