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Spectroscopic Properties of Cu Doped (80-x)Sb_2O_3-20Li_2O-$x$$MoO_3$ Glasses

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The antimony oxide as part of the heavy metal oxide glasses is attractive to researchers in recent years. The new antimony oxide glasses have been successfully synthesized using silica crucible in the ternary system for undoped and doped (80-x)Sb_2O_3-20Li_2O-$x$$MoO_3$ (x = 20, 30 mol.%) doped with 0.1 mol.% CuO_2. The optical characterization in the visible spectral region has been carried out on the doped glasses. The role of the Jahn–Teller effect in Cu doped glasses is determined and the electron transitions in these cations have been determined.

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1. Introduction

Antimony oxide glasses attracted researches in recent years for their low phonon energy, high refractive indices and large optical transmission spectrum. Sb_2O_3 glasses emerges as one major family of HMO glasses [1–4] and appear promising for potential applications in nonlinear optical devices like ultrafast optical switches, power limiters and broad band optical amplifiers. The crystals, glasses and glass ceramics containing cupreous ions are considered as 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 bluish green color due to the presence of Cu^{2+} ions in octahedral coordination and without color if copper is in monovalent oxidation state. Our work was designed to investigate the effect of copper of the changing glass composition on the optical absorption.

2. Experimental details

These glasses were synthesized by conventional method in the ternary system (80-x)Sb_2O_3-20Li_2O-$x$$MoO_3$ doped with 0.1 mol.% of NiO. Starting materials used for the preparation of glasses are commercial products: Sb_2O_3 (Acros 99%), MoO_3 (Aldrich 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 region consists of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a polarizer, sample holder, and a Hamamatsu S2281-01 detector.

3. Results and discussion

The absorption band around 565 nm is due to the transition $Sb^{3+} \rightarrow Sb^{5+}$ in the pure glass 80$Sb_2O_3$20Li_2O

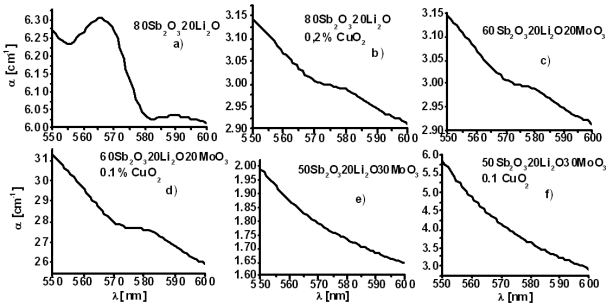

Fig. 1. The absorption spectra of pure and Cu doped glasses in the spectral region 550–600 nm.

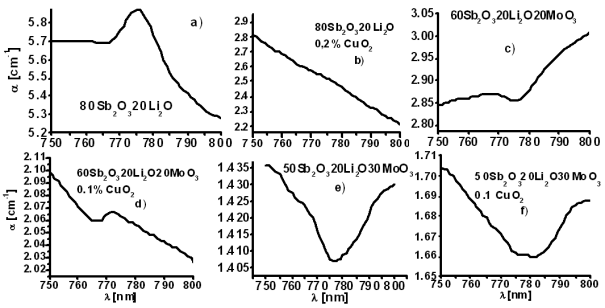

Fig. 2. The absorption spectra of pure and Cu doped glasses in the spectral region 750–800 nm.

(Fig. 1a). The cupreous spectral structure appears around 580 nm (Fig. 1b).

When the concentration of Mo ions increases the cupreous absorption band does not appear (Fig. 1e,f). The other spectral maximum around 777 nm (Fig. 2a) expands in Cu doped glass (Fig. 2b) and it traverses in minimum when Mo ions are inculcated in the glasses (Fig. 2c). When the concentration of Mo increases this minimum is deeper (Fig. 2e,f). The optical absorption spectra of Cu^{2+} ions in (80-x)Sb_2O_3-Li_2O-$x$$MoO_3$ glasses

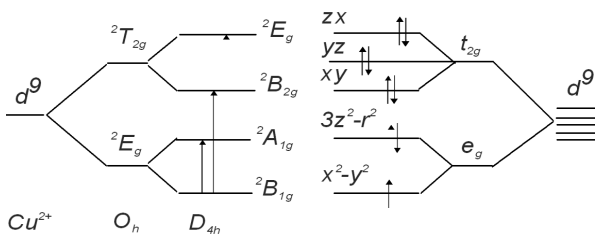

Fig. 3. The energetic diagram of the $3d$ electron transitions in Cu^{2+}.

are shown in Figs. 1 and 2. A broad absorption band in the visible spectral region was observed for the samples. The first maximum in this band is observed around 580 nm and the second one is situated around 777 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 12870 cm^{-1} is due to the overlap of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions (Fig. 3). We attribute the observed maximum at 17241 cm^{-1} to the $^2B_{1g} \rightarrow {}^2E_g$ transition in the tetragonal symmetry (Fig. 3). 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 unequivalency 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.

4. Conclusion

Cu doped glasses in (80-x)Sb_2O_3-20Li_2O-$x$$MoO_3$ has been synthesized and optical characterization has been done. Two asymmetric bands occurred around 12870 cm^{-1} and 17241 cm^{-1}. The first band can be attributed to the overlap of $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions of Cu^{2+} in hexagonal symmetry and the second band is attributed to the $^2B_{1g} \rightarrow {}^2E_g$ transition in the tetragonal symmetry.

Acknowledgments

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References

[1] M.T. Soltani, A. Boutarfaia, R. Makhloufi, M. Poulain, *J. Phys. Chem. Solids* **64**, 2307 (2003).

[2] P. Petkova, M.T. Soltani, S. Petkov, V. Nedkov, *Acta Phys. Pol. A* **121**, 152 (2012).

[3] M.G. Brik, I.V. Kityk, K. Ozga, A. Slezak, *Physica B* **406**, 192 (2011).

[4] M. Luo, Y. Jiang, Ch. Xu, X. Yang, A. Burger, N.G. Giles, *J. Phys. Chem. Solids* **67**, 2596 (2006).

[5] R.E. de Araujo, Cid.B. de Araujo, G. Poirier, M. Poulain, *Appl. Phys. Lett.* **81**, 4694 (2002).

[6] J. Minelly, A. Ellison, *Opt. Fiber Technol.* **8**, 123 (2002).

[7] R. Noks, A. Gold, *Symmetry in Solid State Physics*, Science, Moscow 1970, p. 227.

[8] M.C.M. O'Brien, in: *Proc. 1st Int. Conf. Jerusalem*, Vol. 1, 1962, p. 322.