International Journal of Engineering, Science and Mathematics
Vol. 10 Issue 2, February 2021,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

OPTICAL ABSORBANCE STUDIES OF TRANSITION METAL OXIDES CONTAINING LITHIUM BOROSILICATE GLASSES

Thomas Philip

Department of Physics, Hislop College, Nagpur – 440 001, India
Email:thomasphysics296@gmail.com

KEYWORDS:

: UV-Visible absorbance; optical filters;

ABSTRACT

The glass samples represented by general formula $30LiO_2$: (70-X) $(6/7B_2O_3:1/7SiO_2)$: XTMO (X=0, 0.05, 0.1) were synthesized by conventional quenching technique. The TMOs i.e., Cr_2O_3, MnO_2, Fe_2O_3 and Co_3O_4 were added at the cost of both formers. The study of optical absorbance of the glasses has been carried out. The UV-Visible absorbance of spectra has been studied by using the Fiber optic spectrometer. The observed absorbance bands are typical of the transition metal added to the glass. The optical absorbance results indicate that the glasses containing chromium, manganese and cobalt have a good potential to be developed as optical filters for specific wavelengths in the visible range.

1. INTRODUCTION

Compounds of transition metals and rare earth , giving colouring mechanism, are commonly used as glass dyes. The base glass structure and the electron structure of the transition metal ions determines the colour of the glass. Transition Metal ions are also used as a probe of the glass structure [1-3]. The UV/VIS spectroscopy is a simple experimental technique for the study of colored glasses. The valences and coordination of transition metals in glass can be understood by the analysis of electron spectra.

The absorbance of light has been studied by comparing the intensities of light passing through the sample before (I_0) and after (I). The ratio of I/I_0 is called the transmittance. When the transition metal oxides are added into the base material, the molecular structure is changed. The molecular formulation of the transition metal oxide is significant for the optical absorbance study. In general three types of energies are considered. i.e. Electronic, vibrational and rotational energies of the molecule. For electronic transition, high energy photon is required to excite a molecule from lower to higher level. Comparatively lower energies are required for excitation in vibrational and rotational levels. Vibrational and rotational levels are more closely spaced.

The plot of absorbance against the wavelength of the incident radiation is expected that it should show sharp lines. Each line should occur when an incident photon of energy exactly matches with the energy corresponding to the line in the spectrum. Instead of sharp lines, it is found, in practice, few humps. It shows that the molecule is absorbing radiation over a band of wavelengths. The reason for this band can be attributed, rather than line absorption, to simultaneous change between many vibrational levels along with electronic level transitions. The vibrational level can also be associated with smaller rotational changes. The rotational transition energies fill the gaps in the vibrational structure.

In the present work, the optical absorbance was measured in the wavelength range from 200 nm to 1000 nm [4-5].

2. EXPERIMENTAL

The glass studied in the present work represented by the general formula $30Li_2O$: (70-X)(6/7 B_2O_3 : 1/7 SiO_2) : XTMO (X=0, 0.05, 0.1). The TMOs are Cr_2O_3, MnO_2, Fe_2O_3 and Co_3O_4. The precursors were taken in the molar ratio and thoroughly mixed in acetone using agate mortar and pestle. The mixture was kept in platinum crucible and introduced in the muffle furnace. The temperature of the furnace was maintained at 40^0C above the melting temperature of the material. It was maintained at this temperature for 2 hours for homogenization of the melt. The homogenous melt was quenched in the metallic mould to form glass. The finely polished samples were used for optical absorption studies. the Avaspec Avantes fiber optic spectrometer system is used for the optical absorbance measurement of the samples.

3. RESULTS AND ANALYSIS

The Fig. [1] shows the optical absorbance spectrum of Cr_2O_3 containing glass samples. The Chromium containing glasses have been termed as IB series. The absorbance spectrum consists of strong absorption band in the UV range and another absorbance band centered around 630 nm. Similar results have been reported in the literature for lithium and sodium silicate glasses containing chromium oxide by Terczynska-Madej et al (6). According to them, a very strong absorption in the UV range indicates that it is not d-d absorption.

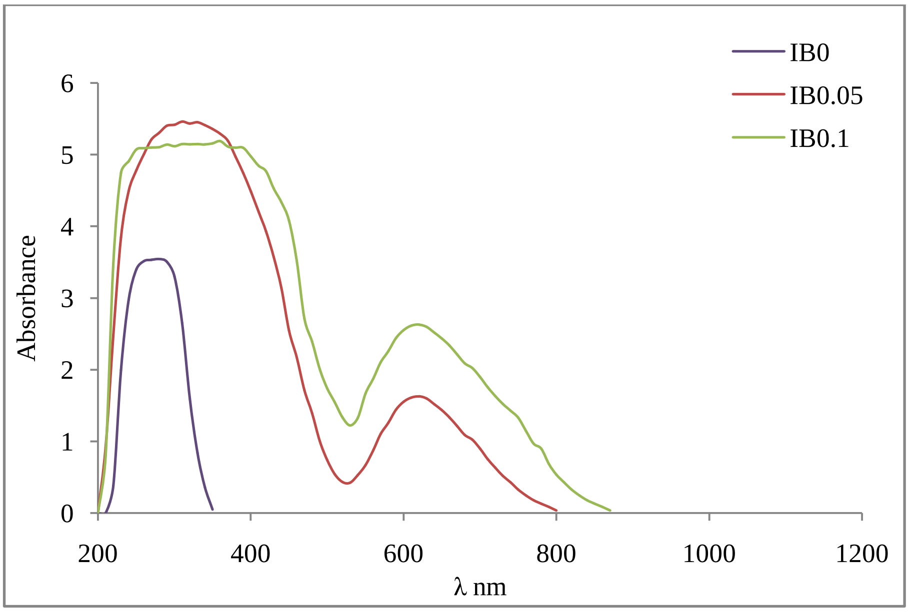

Fig. 1. Absorbance spectra for glass samples containing Cr_2O_3

This absorption can be connected with the presence of chromium ions in the higher valence state, probably as Cr^{5+} (7-10) and /or Cr^{6+} ions(11). The observed absorption bands in the visible range of spectrum can be associated with Cr^{3+}. It has been reported in the literature that the octahedral forms of Cr^{3+} ions show two broad absorption bands due to the transition from the $4A_{2g}$(F) ground state to $4T_{2g}$(F) about 660nm and 4T1g(F) about 450nm excited states (12-13). The $4T_{1g}$(F) band is probably masked by strong UV absorption.

The Fig.[2] shows the optical absorbance spectrum of MnO_2 containing glass samples. The Manganese containing glasses have been termed as IIB series. The UV/VIS absorbance spectrum consists of UV absorption and a broad visible absorption about 450-520 nm. Manganese can be present in the glass usually as divalent or trivalent ions. But it is also possible to exist as Mn^{4+} ions (14). Divalent manganese (d^5 configuration) in octahedral coordination gives only weak absorption bands around 470nm corresponding to the ${}^6A_1$(S) to ${}^4T_1$(G) transition (15). Simialr absorption was reported in Zinc lead borate glasses. Trivalent manganese ions have d4 configuration which gives absorption band around 470-500 nm corresponding to a d-d transition ${}^5E$ to ${}^5T_2$ [16]. The intensity of this band is higher than that of the band derived from Mn^{2+}. in the case of Mn^{4+} ($3d^3$ configuration) the band around 450 nm occurs corresponding to the ${}^4A_2$ to ${}^4T_2$

transition. The band at 470-520 nm observed in the spectra of the glasses in this work may be attributed to Mn^{3+} ions in octahedral coordination with oxygen ions.

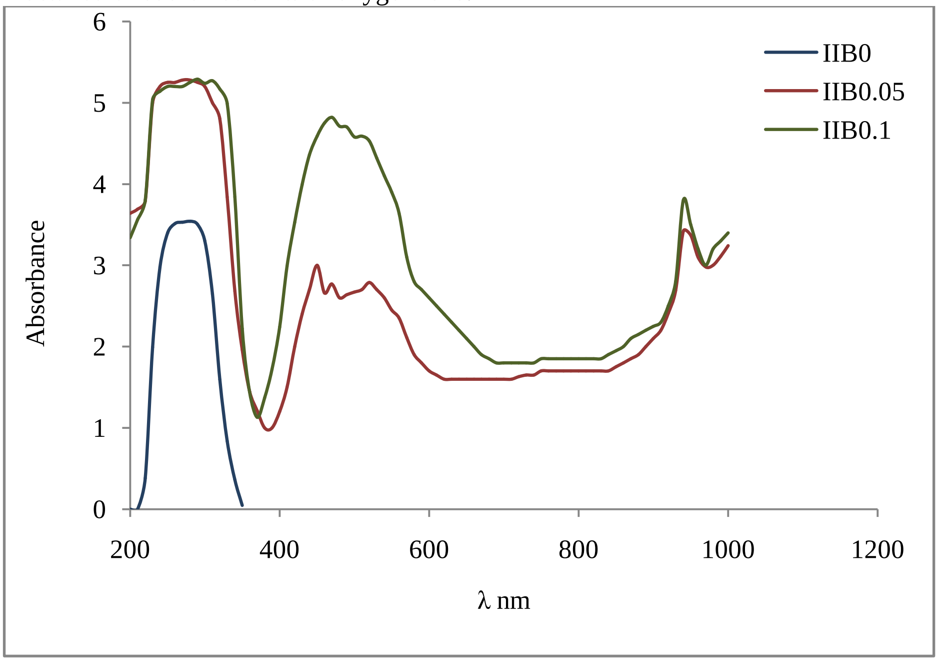

Fig. 2. Absorbance spectra for glass samples containing MnO_2

The band at 470-520 nm observed in the spectra of the glasses in this work may be attributed to Mn^{3+} ions in octahedral coordination with oxygen ions. Similar results have been reported in the literature (17). The intensity of this band can mask any weak absorption bands which may arise from Mn^{2+} ions as well as the band derived from Mn^{4+}.

The Fig. [3] shows the optical absorbance spectrum of Fe_2O_3 containing glass samples. The Fe containing glasses have been termed as IIIB series.

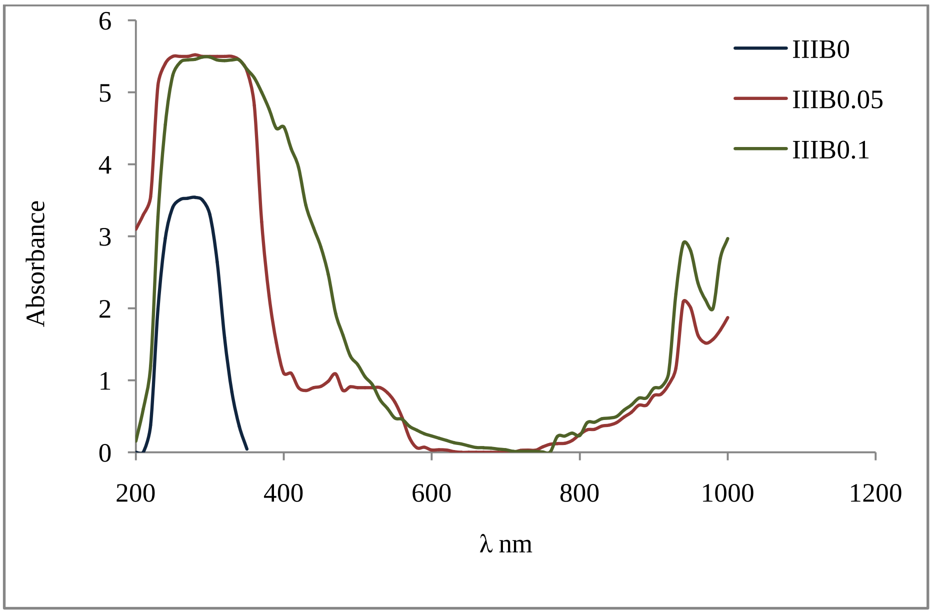

Fig. 3. Absorbance spectra for glass samples containing Fe_2O_3

The addition of Fe_2O_3 in the glass samples give a prominent UV absorption, a broad absorption of low intensity in visible range 400-570 nm. It has been reported [18-20] that two weak absorption bands occur in iron doped glasses at 410 nm and 520 nm. It appears that these two weak peaks are also seen in the present work, but they are very weak. The broadening of UV absorption band is also observed. Similar results have been reported (21) in the sodium borosilicate glasses containing Fe_2O_3. They have attributed this broadening of UV absorption band to possible presence of one site of both iron species Fe^{2+} and Fe^{3+}. (22-23)

The Fig. [4] shows the optical absorbance spectrum of Co_3O_4 containing glass samples. The cobalt containing glasses have been termed as IVB series. In the spectra of these glasses, the absorption band in the range 520-640 nm in the visible region is observed. It has been reported that cobalt usually occurs as divalent ion, Co^{2+} in octahedral and/or tetrahedral symmetry (24-25) in glasses, but in sodium silicate glasses having sodium contents greater than 40% by weight, cobalt can also be obtained in the trivalent state. For Co^{2+} ion with the d7 configuration in the octahedral environment, the transition $4T_{1g}(F)$ to $4T_{1g}(P)$ is attributed to the main band at 540 nm. On the other hand, cobalt ion ions in the same oxidation state but in tetrahedral coordination sphere are reported to give a spectrum consisting of a broad, intense band at 605-667 nm with a small shoulder at 540 nm (26). The transition related to this tetrahedral band is assigned as $4A_2(F) – 4T_1(P)$ (27). In the case of presence of Co^{3+} in octahedral symmetry the band at 590 nm attributed to $1A_{1g} – 1T_{1g}$ transition (28).

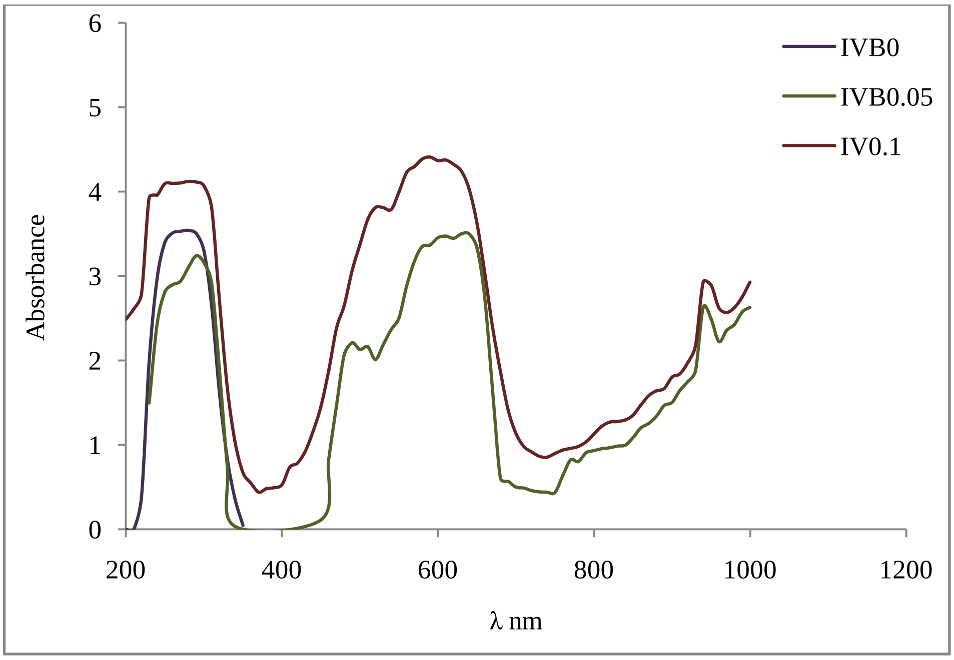

Fig. 4. Absorbance spectra for glass samples containing Co_3O_4

The absorption at different identified band can be assigned to cobalt ions Co^{2+} in tetrahedral and Co^{2+} in octahedral coordination, because the band corresponding to these local states of Co^{2+} are closely located in the spectrum range (29). In this spectral range the band at about 595 nm derived from Co^{3+} in octahedral symmetry(30).

CONCLUSION

It can be concluded from the optical absorption studies that the glasses containing chromium, manganese and cobalt have good potential for being developed as optical filters of specific wavelength in the visible region.

REFERENCES

[1] H. L. Tuller, D.P. Button, D. R. Uhlmann, J. Non-Cryst. Solids, 4 (1980) 93.
[2] J. A. Duffy, Charges on metal ions in glasses, Solid State Ionics, 105 (1998) 87-90.
[3] C. Mercier, G. Palvit, L. Montagne, C. Follet-Houttemane, A survey of transition-metal containing phosphate glasses, C.R.chimie, 5 (2002) 693-703.

[4] K. Morinaga, T. Murata, M.Torisaka, H.Takeba, Compositional dependence of the valency state of Cr ions in oxide glasses, J. Non-Cryst. Solids 220 (2-3) (1997) 139-146.
[5] G. Calas, O. Majerus, L. Cormier, Crystal field spectroscopy of Cr^{3+} in glasses: Compositional dependence and thermal site expansion, Chem. Geol., 229 (2006) 218-226.
[6] A. Terczynska-Madej, K. Cholewa-Kowalska, M.Laczka, Optical Materials 32 (2010) 1456-1462.

[7] V. K Deshpande, Thomas Philip, IOP Conf. Series: Materials Science and Engineering 2 (2009)012042.

[8] O. Cozar, I. Ardelean, I. Bratu, G. Ilonca, S. Simon, EPR, IR, and Magnetic susceptibility studies of xCr_2O_3 (1-x)[$2B_2O_3$*Li_2O] glasses, Solid state Commun., 86 (9) (1993) 569-572.

[9] J. Wong, C. A. Angell, Application of spectroscopy in the study of glassy solid II. Infrared, Raman, EPR and NMR spectral studiem, Appl. Spectr.Rev, 4 (2) (1971) 155-232.

[10] J. Wong, C.a. Angell, Glass structure by spectroscopy, Marcel Decker, New York, 1976 (chapters 6 and 9).

[11] S. R. Ramanan, D. Ganguli, Spectroscopic studies of Cr-doped silica gels, J. Non-Cryst. Solids 212 (1997) 299-302.

[12] Y.Tanabe, S. Sugano, On the absorption spectra of complex ions, J. Phy. Soc, Jpn, 9 (1954) 753-766.

[13] U. Fano, Effects of configuration interaction on intensities and phase shifts, Phys. Rev., 124 (6) (1961) 1866-1878.

[14] M.Yamashita, Z.Yao, Y. Mastumoto, Y. Utagawa, K. Kadano, T.Yazawa, X-ray irradiation-induced coloration of Manganese in Soda-lime silicate glass, J. Non-Cryst. Solids, 333 (2004) 37.
[15] S. Zhang, H. Xia, J.Wang, Y. Zhang, Growth of Mn^{2+}, Co^{2+}, and Ni^{2+}-doped near stoichiometric $LiNbO_3$ by Bridgman method using K_2O flix, J. Alloys Compd., 463 (2008) 446-452.
[16] M.Yamashita, Z.Yao, Y.Matsumoto, Y.Utagawa, K.Kadono, T.Yazawa, X-ray irradiation-induced coloration of manganese in soda-lime silicate glass, J. Non-Cryst. Solids 333 (2004) 37-43.
[17] N. W. Barnett, B. J. Hindson, P. Jones, A.S Trevor, Chemically induced phosphorescence from manganese (II) during the oxidation of various compounds by manganese (III), (IV) break and (VII) in acidic aqueous solutions, Anal. Chim. Acta, 451 (2002) 181-188.
[18] B. Dutta, N.A. Fahmy, I. L. Pegg, J. Non-Cryst. Solids 351 (2005) 2552.

[19] W. Hui, K. Xiao-Yu, D. Dong, T. Xiao-Ming, Y. Xiong, Chem. Phys. 330 (2006).

[20] I. Fontana, A. Lauria, G. Spinolo, Phys. Status Solid, (b) 244 (2007) 4669.

[21] F. H. EIBatal, M. S. Selim, S.Y. Marzouk, M. A. Azooz, Physica B, 398 (2007) 126.

[22] G. Concas, F. Congin, E. Manca, C. Muntoni, G. Pinna, J. Non-Cryst. Solids, 192/193 (1995) 175.

[23] R. P. Sreekanth Chakradhar, A. Murali, J. Lakshmara Rao, J. Alloys Compds., 281 (99) (1998) 99.

[24] X. L. Duan, D. R.Yuan, X. F.Cheng, X.Q.Wang, Z. M.Wang, D. Xu, M. K. Lv, Optical absorption of Co^{2+}-doped silica gel derived glasses, Opt.Mater., 23 (2003) 327-330.

[25] X. Duan, D.Yuan, X.Cheng, Z. Liu, X. Zhang, Preparation and optical properties of Co^{2+} doped Li_2O-Ga_2O_3-SiO_2 glass ceramic, J. Alloys Compd., 453 (2008) 379-381.
[26] G. Lakshminarayana, S. Buddhudu, Spectral analysis of Mn^{2+}, Co^{2+}, and Ni^{2+}, B_2O_3-ZnO-PbO glasses, Spectro chem. Acta A, 63 (2006) 295-304.
[27] J. A. Duffy, Bonding, Energy Levels and Bands, Longmans, London, 1990.

[28] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford,1985.

[29] A. Thulasiramude, S. Buddhudu, Optical Characterization of Mn^{2+}, Ni^{2+}, and Co^{2+} ions doped Zinc lead borate glasses, J. Quant. Spectr. Radiat. Transfer, 102 (2006) 212-227.
[30] J. K. Kwang, Y. Ran Park, Optical Investigation of Charge-Transfer transitions in spinel Co_3O_4, Solid State Commun., 127 (2003) 25-28.