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Research Article

PREPARATION AND CHARACTERIZATION OF TRANSITION METAL OXIDE DOPED BORATE GLASSES

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ABSTRACT

The transition metal ions such as Copper, Silver and Titanium when dissolved in B_2O_3 glass matrix, even in very small quantities, influence the properties very strongly. In the present study Borate Glasses doped with different transition metals have been prepared in laboratory by using Melt Quench Technique. The absorption spectra of the prepared samples have been obtained by using UV/Visible spectroscopy. The Band-Gap Energy (E_g) values are obtained by using Tau's Plots. The significant increase in E_g values from 2.60 to 3.18 eV is observed. A transmission window is observed in the spectra of Cu-doped glass sample which indicates the possibility of large number of applications in the field of nonlinear optics. An increase in the density values from 4.851 to 5.038 gm/cm^{3}is observed with the addition of TMOs having higher atomic number.

INTRODUCTION

Over the past few years, the study on the role of transition metal ions on the physical properties of various glass systems has been the subject of a great deal of interest. These ions are being extensively used in the present days to probe the glass structure since their outer d-electron orbital functions have broad radial distribution and also possess a highly sensitive response to the changes in the surrounding actions. Glasses containing copper as the main component are of increasing interest due to their semi-conducting properties and many other potential applications. The electronic structure of the copper atom is [Ar] $3d^{10}$ $4s^1$; five d orbital occupied for the cuprous ion and it does not produce the colouring, while Cu^{2+} ions create colour centres and create blue and green glasses with an absorption band in the visible region. Glasses doped with transition metals have found a place in the new laser and optical filter applications. These Glasses have attracted a great deal of attention because of the capability of the ions to exist in more than one valence states enabling electrical conduction to occur by the movement of carriers from lower to higher valence state. The transition metal ions (TMIs) in the oxide glasses exist in multivalent oxidation states in glassy matrix exhibiting interesting optical, semiconducting and magnetic behaviours. TMIs doped glass materials are expected to be promising candidates as gain media for ultra-broadband optical fibre amplifiers, tuneable lasers and ultra-short pulse lasers in telecommunication. This is because of the dominance of non-radiative losses over the relaxations of excited states of transition metal ions/lasing spices in these materials. In glasses, copper ions exist in two stable ionic states viz., monovalent Cu^+ ions (cuprous) which does not produce colouring for the glass samples, divalent Cu^{2+} ions create colour centres' that produces blue and green glasses. The colour of the glass depends on the Cu^{2+} content, its specific coordination, composition and basicity of the glass. Copper ions have strong bearing on electrical and optical properties of glasses. These ions subsist in different surroundings (ionic, covalent) in glass matrices. The content of copper in different environments existing in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. [1-4].

Titanium (TiO_2), as a member of 3d TMO has received considerable attention since many titanium compounds are nontoxic and almost all compounds in the environment transform titanium into nontoxic titanium dioxide [5]. In recent years silver doped sodium borate glasses have attracted great attention because of their valuable optical properties and high

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value of ionic conductivity. They are considered to have potential applications in solid state batteries and electrochemical devices [6,7]. Glasses containing high concentration of transition metal ions are electronic conductors [8,9]. This classifies them as a form of amorphous semiconductors.

Because of the documented or potential function of silver in photo-chromic, photosensitive, dosimeter and semiconductor glasses, extensive studies have been made on glasses in which traces of silver have been incorporated. The state of silver in these glasses has been studied by several researchers. Wey stated that if a small amount of silver oxide (0.1% Ag_2O) is introduced into silicate glass, Ag^+ ions participate in the glass structure in a fashion similar to that of Na^+ ions due to the similarity of their charge and size. Silver however, has much lower ionization energy than sodium and, therefore, is more easily reduced. Electron spin resonance experiments have shown that the silver ion, Ag+, is capable of trapping both types of charge carriers, electrons as well as holes, becoming either the neutral species $Ag^{+,-}$ or $Ag^{+,+}$ respectively [10,11].

Experimental Details

Glass Sample Preparation: For the present study, compositions chosen are:
$65H_3BO_3$ - 25PbO - $9NaHCO_3$ - $1TiO_3$
$65H_3BO_3$ - 25PbO - $9NaHCO_3$ - 1CuO
$65H_3BO_3$ - 25PbO - $9NaHCO_3$ - $1AgNO_3$

Analytical grade reagents of H_3BO_3, PbO, $NaHCO_3$ and CuO/$AgNO_3$/TiO_3 chemical powders in appropriate amounts were weighed by using digital electrical balance and thoroughly mixed in mortar and pestle. The batch is then transferred into silica crucible and heated in muffle electric furnace to melt them for an hour at 850^0C. The temperature of the muffle furnace was increased in steps of 50°C. The melt was stirred frequently for homogeneous mixing of all the constituents and to reduce the bubble formation. The glass samples were obtained by pouring the molten material in a preheated (at 350^0C) graphite mould. The annealed furnace was turned off after 20min of pouring the sample. The mould was kept in the furnace for 15-16 hours to protect the samples from thermal cracking. As-prepared glass samples are then grinded by using grinding machine. The grades of the emery used are: 400, 600, 800 and1000. The flat surfaces were obtained and the samples were polished by using Ceric Oxide (CeO_2) as fining agent.

Table 1 Nominal Composition, Melting Point, Density and Band Gap Energy of prepared samples.

Sample	Composition(Mol%)	Melting Temp. (^{o}C)	Density (gm/cm^3)	Band Gap Energy, Eg (eV)
Ti	H_3BO_3-PbO-$NaHCO_3$-TiO_2 (0.65 - 0.25 - 0.09 - 0.01)	900	4.851	2.60
Cu	H_3BO_3-PbO-$NaHCO_3$-CuO (0.65 - 0.25 - 0.09 - 0.01)	850	4.923	2.73
Ag	H_3BO_3-PbO-$NaHCO_3$-$AgNO_3$ (0.65 - 0.25 - 0.09 - 0.01)	930	5.038	3.18

Density

The density of the prepared samples at room temperature was determined by using simple Archimedes method using benzene as immersing liquid (ρ_o = 0.876 g/cm^3). The density (ρ) of glass samples was calculated by using relation given below:

$\rho = \rho_o \frac{W_{air}}{W_{air}-W_l}$ where ρ_o is the density of the buoyant
W_{air} isthe sample weights in air
W_l is the sample weight in the buoyant

UV/Visible Spectroscopy

UV spectroscopy follows the Beer-Lambert law,
A=log $\frac{I_o}{I}$
Where A is absorbance
I = intensity of light leaving the sample cell,
I_o = intensity of light incident upon sample cell. From Beer-Lambert law, it shows that larger is the number of molecules of the absorbing light of a particular wavelength, the larger is the extent of light absorption.

The optical band gap was calculated from UV absorption spectra of all prepared glass samples. However, for non-crystalline systems it is customary to plot $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$) in order to find the optical band gap. Using the relation:

$\alpha h\nu = A(h\nu - E_g)^2$
α = 2.303 (A/d) where E_g is the energy band gap
α is the absorption coefficient
dis the thickness of the sample
A is the absorption
$h\nu$ is the photon energy

RESULTS AND DISCUSSION

The density results are given in Table 1. An increase in the density values from 4.851 to 5.038 is observed with the addition of TMO having higher atomic number. UV/Visible absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range [12].

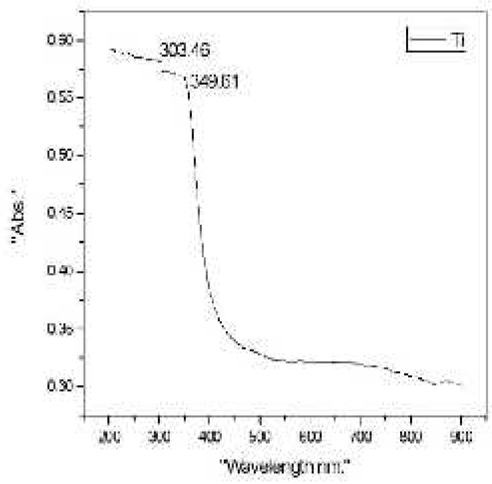

Fig 1 UV/Visible of Ti doped Borate glass sample.

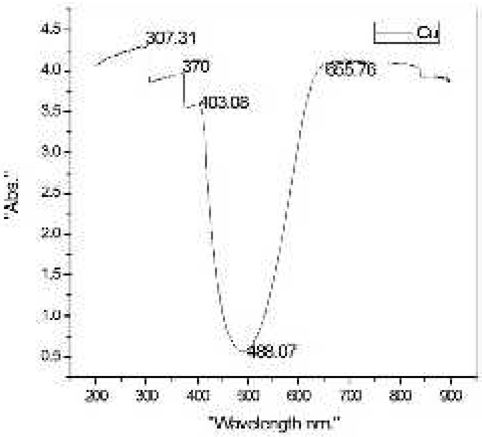

Fig 2 UV/Visible of Cu doped Borate glass sample

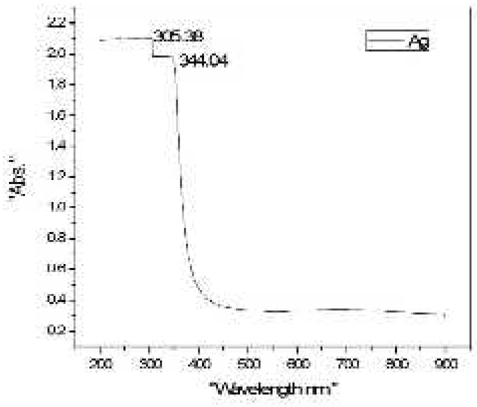

Fig 3 UV/Visible of Ag doped Borate glass sample.

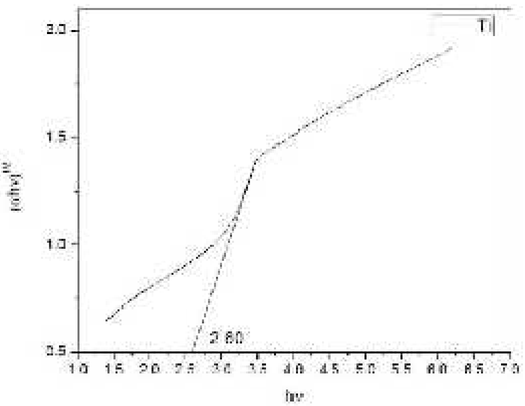

Fig 4 Bandgap of Ti doped Borate glass sample.

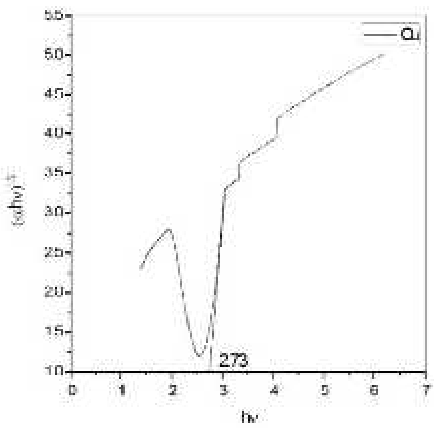

Fig 5 Bandgap of Cu doped Borate glass sample.

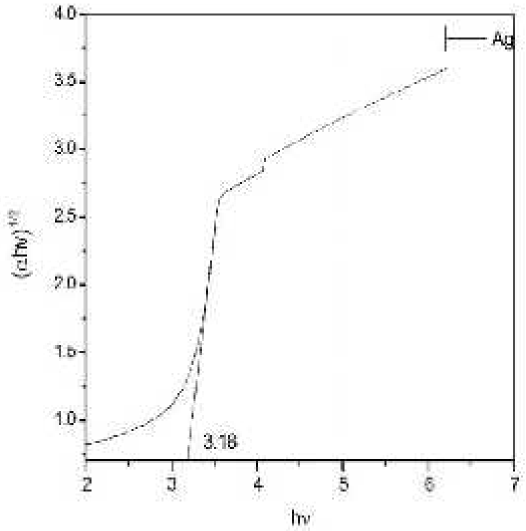

Fig 6 Bandgap of Ag doped Borate glass sample.

Oxide glasses are generally non-conductor of electricity that they act as insulators. Vitreous silica and pure B_2O_3 glasses fall under their category. However, they can be made conductive by the addition of proper modifier or by doping. Fig.1 gives the UV/Visible absorption spectra of Ti doped Borate glass sample, Fig.2 and Fig. 3 gives the UV/Visible absorption spectra of Cu and Ag doped Borate glass sample respectively. The observed results in Cu doped glass are very interesting. There is a transmission window range from 400-600 nm wavelengths. This is unique property which indicates the application of this glass for selective absorption/transmission of radiations. Fig.4 is a Tau's Plot which gives the band gap of Ti doped borate glass sample. Similarly Fig.5 and Fig. 6 give the band gap of Cu and Ag doped borate glass samples respectively. These results are tabulated in Table 1. There is a significant change in the band gap energy values of different glass samples. The conductivity results are Ti> Cu > Ag. The electro negativity values are Ti (1.54) < Cu (1.90) Ag (1.93) and the ionic radius are Ti< Cu < Ag.

CONCLUSIONS

- TMO (Ti-22, Cu-29 and Ag-47) doped lead borate glasses have been successfully made in lab by using melt quenching technique.
- The impact of these TMO's on the different properties of as prepared glasses have been analyzed by using UV/Visible spectroscopy.
- The Band-Gap Energy increases as: [Ag >Cu>Ti].
- Density results for [Ti, Cu, Ag] are [Ti< Cu < Ag].
- Selective transmission window range from 400-600 nm has been found in Cu-doped sample.

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