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Optical Properties of Microwave Prepared Glasses Containing Manganese Ions

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Abstract— Developments of new routes for synthesis of solid materials are an integral part of material science. Microwave associated synthesis is much faster, cleaner and energy efficient than conventional methods. Glasses with general formula $xMnO_2$ -2PbCl₂-(98-x)[0.9NaPO₃-0.1PbO] is prepared by microwave method. The samples were characterized by powder X-ray diffraction. Optical absorption, Photoluminescence spectra of these glasses has been examined. The absorption spectrum exhibits a peak at 511nm and this has been attributed to the ${}^5E_g \rightarrow {}^5T_{2g}$ allowed transition. The common manganese ions found in oxide glasses are Mn^{2+} and Mn^{3+} , although higher oxidation are known to exist. Mn^{2+} has $2d^5$ configuration and all transitions are spin forbidden and therefore of low intensity. Photoluminescence spectra reveal that divalent manganese in its octahedral environment emits around 558 nm. The observation of emission around 558 nm in the present glass indicate octahedral coordination and has been attributed to the ${}^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ spin forbidden transition of Mn^{2+} ions. From the UV/Visible absorption edges, the optical band gap energies were calculated. With increase in MnO_2 content the optical band gap energies decreases.

Keywords-Microwave synthesis; Photoluminescence; Optical band gap; Coordination

1. INTRODUCTION

The fast development of photonic technology needs suitable and efficient materials for photonic devices like high power lasing materials and fiber optic non linear materials[1]. Inorganic glasses are the most suitable and promising materials for the above said devices [2] due to ease of synthesis and its dependence on doping concentration. Manganese ions exist in different valence states with different co-ordinations in glass matrices. The content of manganese in different co-ordinations in different valence states exist in the glass depends upon the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength and mobility of the modifier cat ion etc. [3]. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous coordination, systems. Studies of the bonding characteristics and covalence state of transition metal ions in glasses are very helpful in understanding the structure of the glassy state. Changes in the chemical composition of glass may change the local environment of the transition metal ion incorporated into the glass, leading to ligand field changes, which may be reflected in the optical absorption spectra. So, optical absorption is one of the important tools to understand the structure of glassy state. Transition metal oxides dissolve readily in phosphate glasses giving characteristic coloration [4] which sensitively depends on the oxidation state and the coordination of the transition metal and arises mostly from d-d electronic transitions. However, very few studies on the structure and the physical properties of transition metal-doped alkali phosphate glasses have been performed so far [5, 6]. Divalent manganese ions play an important role as active centers in inorganic phosphors, mainly for lighting applications. They exhibit a 3d⁵ electronic configuration and photoemission usually occurs due to the transition ${}^{4}T_{1}(G) \rightarrow {}^{6}A_{1}(S)$. Therefore, the position of the emission band is strongly dependent on the field strength of the surrounding lattice. Typically, the emission peak lies between about 500 and 700 nm with a bandwidth of several tens of nanometers [7-9]. As a consequence, fluorescence from Mn^{2+} dopants can be used, for instance, for probing coordination numbers or other structural data in both glasses and crystalline materials [7, 10]. Study of optical absorption and particularly the absorption edge is one of the useful methods to investigate optically induced transitions and obtain information about band structure and energy gap of both crystalline and non-crystalline materials. A wide range of controllable optical, mechanical, thermal and physical properties make glasses the most useful class of

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materials in which the form and function can be combined in accordance with requirement.

2. SYNTHESIS OF GLASS

Microwave synthesis of materials are gaining importance because, this method is much faster, cleaner, energy efficient and economical than the conventional methods. The energy transfer from microwaves to reactants occurs either through resonance or through relaxation. Melting and homogenizing in conventional methods leads to undesirable decomposition, oxidation/ reduction of reactant oxides, loss of materials by evaporation (which leads to oxygen loss). Microwave synthesis requires at least one of the reactant must be microwave susceptor. Most of the ionic materials are microwave susceptors, since ion current cause coupling with microwaves [11-12]. The transition metal oxide containing glasses of the system The glass samples having the general chemical formula x $MnO_2 - 2 PbCl_2 - (98-x) [0.9NaPO_3 - 0.1]$ PbO] with x = 0, 0.5, 1, 1.5, 2, 2.5 and 3 mol% have been prepared by microwave heating technique using analar grade sodium dihydrogen phosphate (NaH₂PO₄), Lead oxide(PbO), Lead chloride (PbCl₂) and Manganese dioxide (MnO_2) as starting materials. An appropriate quantity of weighed chemicals was mixed thoroughly ground to homogenize the mixture. The mixture is taken in a silica crucible and kept inside a domestic microwave oven operating at 2.45 GHz and at a tunable power level (up to a maximum of 850 W). Within 8-10 min of microwave exposure a good homogeneous melt was obtained, which was immediately quenched between brass blocks. The silica crucible was found to remain clean and unaffected during the short duration of melting. The glass was annealed in a muffle furnace for 1 hour at 200° C to remove thermal strains that could have developed during quenching. The samples were preserved under anhydrous atmosphere. The densities of the investigated glasses were measured at room temperatures by applying Archimedes principle, with toluene as the immersing liquid, according to the equation

$$\rho = \left(\frac{W_a}{W_a - W_L}\right) \rho_L$$

Where W_a and W_L are weights of the glass free from cracks and air bubbles in air and in liquid, respectively. ρ_L is the density of toluene (0.860 gm cm⁻³). The relative error in this measurement is about \pm 0.005g/cm³). Molar volume was calculated for each sample using the relation $V = \frac{M}{\rho}$, where M is the molecular weight calculated

according to the relation $M = \sum_{i} x_i M_i$, where x_i is the mole fraction of the component oxide *i* and M_i is its molecular weight. The uncertainty in molar volume is \pm

0.3 cm³/mol. The amorphous nature of the glass samples was confirmed using (XRD) (Model: Rigaku DMAX- IC employing Cu-K radiation). The XRD spectra did not show any sharp peaks, indicating that the samples were amorphous in nature. UV–Visible absorption spectra of synthesized glasses were recorded using Perkin Elmer (Lamda 35) spectrometer in the UV-Vis-NIR region in the range 200 to 1000 nm. Wavelength at room temperature using a Lab. RAM HR (UV) system, which has high spectroscopic resolution and a unique wavelength range capability. Photoluminescence emission spectra of glasses doped with different concentrations of manganese were recorded at 325nm excitation

3. RESULTS AND DISCUSSION

3.1 Density and Molar Volume

Sample codes, composition and molar mass of the samples are shown in table 1. The variation in density and molar volume of the investigated glasses as a function of MnO_2 mol% is shown in the Fig 1. From the figure it is clear that, density of samples increases from 3.10 gm/cc to 3.16 gm/cc and molar volume decreases from 37.85cc to 36.86 cc with the increase of MnO_2 mol% in the glasses. In the glass system MnO_2 mol% is substituted to PbO and NaPO₃.

 Table 1: Sample codes, glass composition and molar mass of samples

Code	Glass composition				Molar
	Mno_2	$PbCl_2$	NaPO ₃	PbO	mass (gm)
MN0	0.0	2	88.20	9.80	117.34
MN1	0.5	2	87.75	9.75	117.21
MN2	1.0	2	87.30	9.70	117.04
MN3	1.5	2	86.85	9.65	116.93
MN4	2.0	2	86.40	9.60	116.75
MN5	2.5	2	85.95	9.55	116.62
MN6	3.0	2	85.50	9.50	116.48

The rate of increase of molecular weight of the samples with the increase in MnO_2 mol% is more



Fig. 1: Variation of p and molar volume with MnO₂ mol%

than the rate of decrease of molecular weight of the samples with the decrease of PbO and NaPO₃ mol% in the samples. Due to this reason, the density of the glass samples increases with increase in MnO_2 mol%. The increase in density is resulted in decrease of molar volume of glass samples with the increase of MnO_2 mol% suggests that the glass network becomes more compact.

3.2 UV- Visible Absorption

The most common manganese ions found in oxide glasses are $Mn^{2+}(3d^5)$ and $Mn^{3+}(3d^4)$ states [13].In cubic crystal field of low to moderate strength, the five d-electrons of Mn^{2+} ions distributed in t_{2g} and e_g orbitals with ground state configuration $(t_{2g})^3$ and $(e_g)^2$. Such a configuration will give rise to the electronic states, ${}^{6}A_{1g}$, ${}^{4}A_{1g}$, ${}^{4}Eg$, ${}^{4}T_{1g}$, ${}^{4}T_{2g}$, ${}^{4}A_{2g}$ and a number of doublet states of which ${}^{6}A_{1g}$ lies deepest according to Hund's rule. As Mn²⁺ ions belong to d^5 configuration are spin forbidden and low intensity absorption bands. In the present glass system a small shoulder like band is observed around 410nm can be assigned to ${}^{6}A_{1G} \rightarrow {}^{4}E_{g}(G)$. Study of optical absorption and particularly the absorption edge is a useful method for the study of optically induced transitions and for evolving information about the band structure and the energy gap for both crystalline and glassy materials. Optical absorption spectra of manganese ion doped with NaPO₃-PbO-PbCl₂ glass is shown in Fig 2. It is observed from Fig 2 that the absorption intensity of the observed bands increase with an increase in MnO₂ concentration. The absorption spectrum exhibits a broad peak at around 511nm and this has been attributed to the ${}^{5}E_{g} \rightarrow {}^{5}T_{2g}$ allowed transition of Mn²⁺ ion. For the absorption region, Mott and Davis proposed the following relation for amorphous materials [14]



Fig. 2: UV Visible absorption spectra of Mn²⁺ in glass system

$$\alpha(v) = B(hv - E_{opt})^n / hv$$

where n= $\frac{1}{2}$ allowed transition gives direct optical band gap, n=2 allowed transition gives indirect optical band gap and B is a constant. By plotting $(\alpha hv)^2$ as a function of photon energy hv, optical band gaps for direct transitions could be found respectively by extrapolating to $(\alpha hv)^2 = 0$ for direct transitions. Similarly indirect band gaps could be estimated by plotting $(\alpha hv)^{\frac{1}{2}}$ as a function of photon energy hv. The typical plots of $(\alpha hv)^2 v/s hv$ for glass samples sample to calculate direct band gaps are shown in fig 3. The absorption coefficient, below and near the edge of each curve was determined at different wavelengths using relation



Fig. 3: Direct band gap graphs of glass system

$$\alpha(\gamma) = \frac{1}{d} \ln\left(\frac{I_o}{I_t}\right)$$

Where I_0 and I_t are intensities of incident and transmitted beams, respectively and d corresponds to thickness of each sample. The variation of direct and indirect band gaps with MnO₂ mol% is shown in Fig 4. From the figure it is obvious that, both the direct and indirect band gaps of glass sample decreases with the increase of MnO₂ mol%. This clearly suggests the fact that, the number of NBO's (Non Bridging Oxygen's) increases with the increase of MnO₂ mol% in glasses.

3.3 PL Studies

The excitation and emission spectra of Mn^{2+} ions in present glass matrix is shown in fig 5. Photoluminescence spectra reveal that divalent manganese in its octahedral environment emits around 558 nm. The observation of emission around 558 nm in the present glass indicate octahedral coordination [15] and has been attributed to the ${}^{4}T_{1g}(G) \rightarrow {}^{6}A_{1g}(S)$ spin forbidden transition of Mn^{2+} ions in octahedral coordination. The excitation spectra exhibit bands characteristics of octahedral coordination of Mn^{2+} ions. According to Orgel diagram of crystalline field provokes a degrease of energetic separation between the excited state and ground state level, as a consequence an increase in the emission is expected.

4. CONCLUSION

The good stabilized glasses have been synthesized by energy efficient microwave method. The decrease in energy band gaps clearly indicated the formation of NBO's in the glasses. The observation of emission around 558 nm in the present glass indicate octahedral coordination and has been attributed to the ${}^{4}T_{1g}(G) \rightarrow {}^{6}A_{1g}(S)$ spin forbidden transition of Mn^{2+} ions in octahedral coordination.



Fig. 4: Optical band gaps with MnO₂ mol%



Fig. 5: Typical Pl Spectrum of 1.5 mol% MnO₂ sample

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