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# Photoluminescence Studies of NaPO<sub>3</sub>- ZnO - MnO<sub>2</sub> Glass System

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Abstract— Manganese doped sodium phospho-zinc oxide glasses of the composition 80-x)NaPO<sub>3</sub>-20 ZnO - xMnO<sub>2</sub> (where x = 1, 3, 5, 7.5, 10 mol%) have been synthesized by energy efficient microwave heating technique. In order to understand the role of manganese in these glasses, the, optical absorption and photoluminescence properties were investigated. The optical absorption spectra were measured in the wavelength range 200 to 900 nm. The optical band gaps were determined. Absorption edge occurred at 500 nm for all MnO<sub>2</sub> concentrations exhibiting a prominent band due to  $Mn^{3+}$  ions in octahedral symmetry. The optical band gap decreases with increasing Transition metal ion ( $Mn^{2+}$ ) concentration and is attributed to the structural changes taking place due to the addition of manganese oxide. Emission intensity increases with increasing dopant concentration and no quenching effects were observed in this concentration range. Photoemission occurs at around 586 nm to 624 nm and the emission is red-shifted for higher  $Mn^{2+}$ concentration and green-shifted for lower concentration. This is attributed to the transition from  ${}^{4}T_{1}({}^{4}G)$  lowest excitation state to  ${}^{6}A_{1}({}^{6}S)$  ground state of 3d electrons in the  $Mn^{2+}$  ion

Keywords—Microwave heating, Optical absorption, Photoluminescence

### 1. INTRODUCTION

Glasses containing transition metal ions have attracted researchers due to their applications in electrochemical, electronic, electro-optic and photo-conducting devices [1-3]. Many 3d-transition metals can exist in more than one oxidation state in glasses [4,5]. Phosphate glasses containing transition metal ions have unique properties which led to many technological applications such as electronic and electro-optical devices [6]. But poor chemical stability, high hygroscopicity and volatile nature of phosphate glasses prevented the technological applications. However, alkali modified phosphate glasses are highly stable, which can be achieved by adding heavy metal oxides into  $P_2O_5$  glass network [7]. Properties of the alkali phosphate glasses are influenced by the distribution of polymeric anions in the network. In view of this, metal oxides such as CaO, MnO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> etc., are added to sodium phosphate glasses for the purpose of modification [8].

Manganese ions have been frequently used as paramagnetic probes to explore the structure and properties of vitreous systems as their ions have a strong bearing on the optical and magnetic properties of glasses.  $Mn^{2+}$  and  $Mn^{3+}$  are well known paramagnetic ions and  $Mn^{2+}$  and  $Mn^{4+}$  are identified as luminescence activators. The content of manganese in different valence states depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength and mobility of the modifier cations. Hence, the structural properties of the glass is expected to be highly interesting.

The optical absorption studies are recognized as powerful tool for probing the local environment of a paramagnetic impurity and mapping the crystal field [9-11]. 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.

Photoluminescence which is actually the emission of light from a specimen under optical excitation helps in deriving additional information about the emitting material and is useful in surface diagnostic as this phenomenon often originates from the surface layer of the material. Divalent manganese ions act as vital centres in inorganic phosphors, mainly for lighting applications. They are found to exhibit a 3d<sup>5</sup> electronic configuration and photoemission generally occurs due to the transition  $^{6}T_{1}(G) \rightarrow ^{6}A_{1}(S)$ . Therefore, the position of the emission band is greatly dependent on the field strength of the surrounding lattice. Mostly, the emission peak lies between about 500 and 700 nm with a bandwidth of several tens of nanometres [11-13]. As a result, fluorescence from Mn<sup>2+</sup> dopants are used for analysing coordination numbers or other structural data in both amorphous and crystalline materials [12,14]. The strong dependence of emission behaviour on host lattice makes the  $Mn^{2+}$  centre a highly adaptable and is an attractive component for the development of novel phosphors that emits in the green-to-red spectral range. In the present study, optical and photoluminescence studies of Sodium

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Phospho - Zinc oxide glasses doped with Manganese (NPZM) glass system synthesized by microwave method are discussed.

#### 1.1 Experimental

The transition metal oxide containing glasses of the system (80-x)NaPO<sub>3</sub>-20 ZnO - xMnO<sub>2</sub> (where x = 1, 3, 5, 7.5, 10 mol%) were prepared by microwave heating technique using analar grade sodium hydrogen phosphate (NaH<sub>2</sub>PO<sub>3</sub>), Zinc oxide (ZnO) and Manganese oxide  $(MnO_2)$  as starting materials. An appropriate quantity of weighed chemicals were mixed and thoroughly ground to homogenize the mixture and kept in a silica crucible inside a domestic microwave oven operating at 2.45 GHz and 850 W. Within 8-10 minutes of microwave exposure a good homogeneous melt was obtained and it was immediately quenched between copper blocks. The silica crucible was found to remain clean and unaffected during the short duration of melting. The glasses were annealed in a muffle furnace for about 2 hours at 200°C to remove thermal strains that could have developed during quenching and the glasses were preserved under anhydrous atmosphere (CaCl<sub>2</sub>).

UV-Visible Absorption spectra of synthesized glasses was recorded using Perkin Elmer (Lambda 35) spectrometer in the UV-Vis-NIR region in the range 200 to 900 nm.

Photoluminescence emission spectra of glasses doped with different concentrations of manganese were recorded at 325nm excitation wavelength at room temperature using a LabRAM HR (UV) system, which has high spectroscopic resolution and a unique wavelength range capability.

#### 1.1.1 Results and Discussion

The composition and code of sodium phosphor-zinc oxide glasses containing  $Mn^{2+}$  ions are listed in Table 1.

Table 1: Code and composition of NPZM glass system

Code	Composition in mol %		
	NaPO <sub>3</sub>	ZnO	$MnO_2$
NPZM1	79	20	01
NPZM2	77	20	03
NPZM3	75	20	05
NPZM4	72.5	20	7.5
NPZM5	70	20	10

*Optical absorption spectra*— Optical absorption spectra of sodium phospho - zinc oxide glasses doped with manganese is shown in Fig.1. The absorption edges are not sharply defined in the investigated glasses and are therefore in accordance with amorphous solids [15]. The absorption edge of the glasses is generally determined by the oxygen bond strength in the network structure of glass. Any change of oxygen bonding in the glass network due to the formation of non-bridging oxygen, changes the characteristic absorption edge. The absorption edge occurred at a wavelength of about 500 nm for all  $MnO_2$ concentrations exhibiting a prominent broad band characteristic of  $Mn^{3+}$ . As seen from the spectra, the absorption edge slightly shifts to lower wavelength when  $MnO_2$  concentration increased. Shift in the position of band maxima might be generally attributed to the ionic radii of cations.



Fig. 1: Optical absorption spectra of (80-x) NaPO<sub>3</sub>-20 ZnO - xMnO<sub>2</sub> glass system

The broad band is assigned to an allowed transition  ${}^{5}E_{g} \rightarrow {}^{5}T_{2g}$ , due to  $Mn^{3+}$  ions being in octahedral symmetry. Another weak but clearly distinguishable band is seen at 410 nm corresponding to  ${}^{6}A_{1g}(S) \rightarrow {}^{4}A_{1g}(G)$  of  $Mn^{2+}$  ions [16]. This band is due to the tetrahedral transition of divalent manganese ion [17]. However, the octahedral band is observed to grow at the expense of the tetrahedral band. The optical absorption of disordered materials follows Tauc's rule (Tauc, Mott and Davis power law). Direct and indirect optical band gaps have been calculated using Davis and Mott [18]. Values of the optical band gap obtained from Tauc's plots are listed in Table 2.

Table 2: Optical band gap (Direct  $E_{di}$  and indirect  $E_{indi}$ ) and Urbach energy ( $\Delta E_o$ ) values of NPZM glass samples.

Glass code	E <sub>di</sub> (eV)	E <sub>indi</sub> (eV)	∆ E <sub>o</sub> (eV)
NPZM1	3.506	3.072	0.261
NPZM2	3.227	2.772	0.300
NPZM3	3.168	2.703	0.328
NPZM4	3.002	2.452	0.335
NPZM5	2.986	2.429	0.370

The optical band gap ( $E_{dir}$  and  $E_{indi}$ ) and Urbach energy ( $\Delta E$ ) values of all the glass samples is listed in Table 2. It is seen from Table 2 that the optical band gap energies ( $E_{dir}$  and  $E_{ind}$ ) decreases and Urbach energy ( $\Delta E$ ) increases with the increase in concentration of manganese ions. This is attributed to the increase in non-bridging oxygen content with the increasing concentration of

 $MnO_2$ . At higher concentrations of  $MnO_2$ ,  $Zn^{2+}$  ions are incorporated into the network forming positions [19]. This can also be attributed to the formation of octahedral structural units which in turn causes an increase in non bridging oxygen atoms.

Photoluminescence- Luminescence is a radiative decay process which involves transitions between the electronic energy levels of the materials. The doped ions in crystalline or amorphous materials often show fluorescence between their electronic energy levels. Transition metal ions and rare earth ions are some of the most common optically active centres. The electronic structure of manganese (3d<sup>5</sup>) comprises of the excited states  ${}^{4}G$ ,  ${}^{4}P$ ,  ${}^{4}D$  and  ${}^{4}F$ . For  $Mn^{2+}$ , the ground state is  $^{6}A_{1}(S)$  and at least five transitions can readily be identified in the optical excitation spectra at 348.9 nm, 360.7 nm, 409.4 nm, 421.9 and 504.4 nm. These correspond to the transitions  ${}^{6}A_{1}(S) \rightarrow {}^{4}E(D), {}^{6}A_{1}(S) \rightarrow {}^{4}T_{2}(D), {}^{6}A_{1}(S) \rightarrow {}^{4}A_{1}(G), {}^{6}A_{1}(S) \rightarrow {}^{4}T_{2}(G) \text{ and } {}^{6}A_{1}(S) \rightarrow {}^{4}T_{2}(G)$  ${}^{4}T_{1}(G)$  respectively . The photoemission generally occurs due to the transition  ${}^{4}T_{1}(G) \rightarrow {}^{6}A_{1}(S)$ . Fig.2 presents a typical photoluminescence emission spectrum obtained at room temperature from the annealed glass samples containing MnO<sub>2</sub>.



Fig. 2: Photoluminescence emission spectrum of Mn doped glass samples.

The emission band showed a peak maximum ranging from 586 nm to 624 nm with increasing concentration of manganese for fixed excitation wavelength of 325nm. The emission spectra of the glass samples recorded at room temperature exhibited an emission peak at 586 nm for 1 Mn mol% doped sample leading to the green PL emission and occurrence of an emission peak at 624 nm for 7.5 Mn mol% doped sample corresponds to red photoemission. The emission spectra are found to vary from green to deep red colour based on the change in ligand field strength.

## 2. CONCLUSIONS

The absorption edge of the glasses is generally resolved by the oxygen bond strength in the network structure of glass. Any variation of oxygen bonding in the glass network due to the formation of non-bridging oxygen, changes the usual absorption edge. Absorption edge occurred at 500 nm for all MnO<sub>2</sub> concentrations exhibiting a prominent band due to Mn<sup>3+</sup> ions in octahedral symmetry. The optical band gap decreases with increasing Transition metal ion  $(Mn^{2+})$  concentration and is attributed to the structural changes taking place with the introduction of manganese oxide. Emission intensity increases with increasing dopant concentration and no quenching effects were observed in this concentration range. Photoemission occurs at around 586 nm to 624nm and the emission is red-shifted for higher  $Mn^{2+}$ concentration and green-shifted for lower concentration. This is attributed to the transition from  ${}^{4}T_{1}({}^{4}G)$  lowest excitation state to  ${}^{6}A_{1}({}^{6}S)$  ground state of 3d electrons in the  $Mn^{2+}$  ion.

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