PHOTOLUMINESCENCE SPECTRA OF LiI-AgI-B_2O_3 GLASSES DOPED WITH MnO

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Abstract: A study of the electrical properties of the glasses is of considerable importance because of the insight it gives into the conduction mechanism process-taking place in them. In fact, the electrical properties of the glasses are to a large extent controlled by the structure, composition, and the nature of the bonds of the glasses. The investigation of the changes in the electrical properties of glasses with controlled variation of chemical composition, doping etc., is of considerable interest in the application point of view. During the last few decades a large variety of inorganic glasses have been developed with an attempt to achieve suitable electrical, optical and mechanical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, and their ability to accept transition metal ions for their use in solid-state devices. Investigations on the spectroscopic properties such as optical absorption, infrared spectra, electron spin resonance and photoluminescence can be used as probes to throw some light on the structural aspects of these glasses. Such studies may facilitate for explanation of pre assessment over the valance states of manganese ions and their coordination in the glass network; such information will facilitate the analysis of the results of electrical properties quantitatively.

Study of electrical properties of solid electrolytes has received wide attention due to their potential applications in solid state ionic devices such as fuel cells, gas sensors, electrochemical capacitors, electro chromic displays, analog devices, cathodes in electro chemical cells, smart windows etc. The conductivity of LiI–AgI mixed glasses especially, has been the subject of extensive investigation in recent years as a quest for new solid electrolytes with super ionic properties. Further, the transition metal ions like Manganese are very interesting ions to probe in the glass networks because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the electrical properties of the glasses to a substantial extent.

Keywords: Methods adopted in recording (a) absorption (b) excitation (c) photoluminescence spectra.

Introduction: In recent years there have been extensive investigations on the influence of manganese ions on electrical properties and other physical properties of various inorganic glass systems that include silicate, borate, arsenate, phosphate, tellurite etc. [1-7]. Manganese ions exist in different valence states with different co ordinations in glass matrices, for example as Mn^{3+} in borate glasses with octahedral coordination where as in silicate and germinate glasses as Mn^{2+} with both tetrahedral and octahedral environment [8]. Both tetrahedral and octahedral Mn^{2+} ions are reported to have exhibited luminescence emission in the green and red regions respectively in several glasses [9-11]. Both Mn^{3+} and Mn^{2+} ions are well known paramagnetic ions. Mn^{3+} ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital where as such anisotropy energy of Mn^{2+} ion is small because its orbital angular momentum is zero.

When LiI-AgI-B_2O_3 glasses are doped with multivalent transition metal ions like manganese mixed electronic and ionic, pure electronic or pure ionic conduction is expected depending upon the composition of the glass constituents

The content of manganese in different environments and in different valence states existing in the glass however 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. Hence, the connection between the state and the position of the manganese ion and the electrical properties of the host glass containing highly mobile ions like Ag^+ and Li^+ is expected to be highly interesting.

Spectroscopic properties viz., optical absorption, ESR and photoluminescence spectra were studied to have some pre-assessment over the valance states of manganese ions and their coordination in the glass network; such information will facilitate the analysis of the results of electrical properties quantitatively.

For the present study, a particular composition (39–x)LiI–1.0AgI–60B_2O_3: *x*MnO with *x* ranging from 0 to 0.8 (in mol%) is chosen.

The detailed compositions are as follows:
Mn_0 : 39 LiI–1.0 AgI–60 B_2O_3
Mn_1: 38.9 LiI–1.0 AgI–60 B_2O_3: 0.1 MnO
Mn_2: 38.8 LiI–1.0 AgI–60 B_2O_3: 0.2 MnO
Mn_4: 38.6 LiI–1.0 AgI–60 B_2O_3: 0.4 MnO
Mn_6: 38.4 LiI–1.0 AgI–60 B_2O_3: 0.6 MnO
Mn_8: 38.2 LiI–1.0 AgI–60 B_2O_3: 0.8 MnO

Spectroscopic Properties: Under the spectroscopic properties (a) optical absorption, (b) electron spin resonance spectra (c) infrared transmission spectra, Raman spectra (d) luminescence *spectra were studied.*

Photoluminescence Spectra: The photoluminescence spectra of the samples were recorded at room temperature on a Photon Technology International (PTI) Spectro fluorometer (Fig 1).This instrument contains auto calibrated quadrascopic monochrometer for wavelength selection and quadracentric sample compartment. The light source is high intensity continuous xenon lamp with high sensitivity TE–cooled InGaAs detector with lock-in amplifier and chopper for noise suppression and an additional emission mono with a 600 groove grating blazed at 1.2 microns. The system provides unmatched NIR luminescence recording capability from 500 nm–2.2 m. The spectral resolution is 0.1 nm.

The brief sketch of the methods employed in recording the absorption, excitation and photoluminescence spectra are shown in Fig 2.

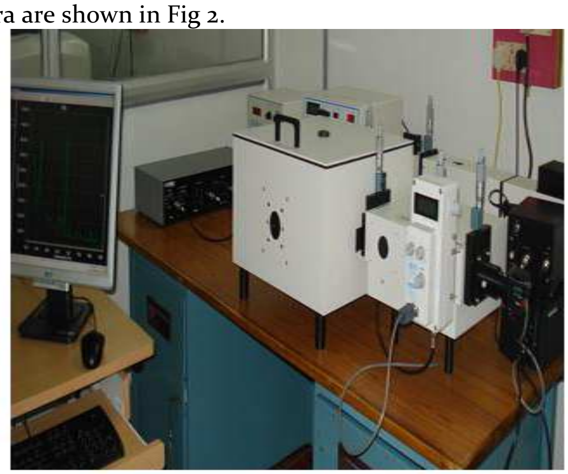

Fig 1: Photon Technology International Fluorescence Spectrophotometer

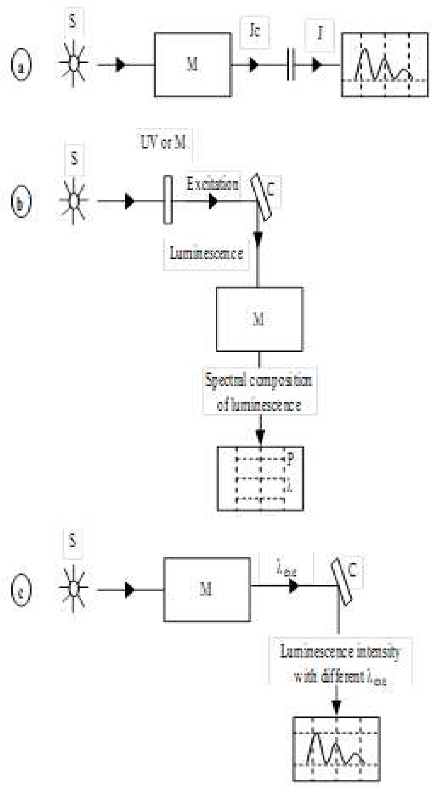

Fig. 2: Brief Sketch of the Methods Adopted In Recording
(A) Absorption (B) Excitation And (C) Photoluminescence

several LiI-AgI-B_2O_3 glasses doped with different transition metal oxides are found
In general it is to be pointed out the data have been taken with the several LiI-AgI-B_2O_3 glasses doped with different transition metal oxides are found to be reproducible with in the accuracies mentioned.

Luminescence Studies: The room temperature fluorescence spectra of LiI–AgI– B_2O_3: MnO glasses excited at the wavelength corresponding their absorption edge are shown in Fig.5.5; the spectrum of glass Mn_1 exhibited two emission bands at about 628 nm and 546 nm assigned to $^4G \rightarrow ^6S$ transitions [12,13]. To be more specific the 628 nm band is attributed to $^4T_{1g}(G) \rightarrow ^6A_{1g}(S)$ spin forbidden transition of octahedrally positioned Mn^{2+} ions where as the green emission band is identified due to $^4T_1$ (G) $\rightarrow$ $^6A_1$ (S) spin allowed transition of tetrahedrally positioned Mn^{2+} ions [14,15].
As the concentration of MnO is increased gradually up to 0.8 mol %, the tetrahedral band is observed grow at the expense of octahedral band. Thus the luminescence studies indicate that as the concentration of MnO increased there is gradual transformation of Mn^{2+} ions from octahedral to tetrahedral positions in the glass network.

Thus the summary of the results of spectroscopic studies is as follows: the manganese ions do exist in both Mn^{2+} and Mn^{3+} states in LiI–AgI– B_2O_3 glass network.

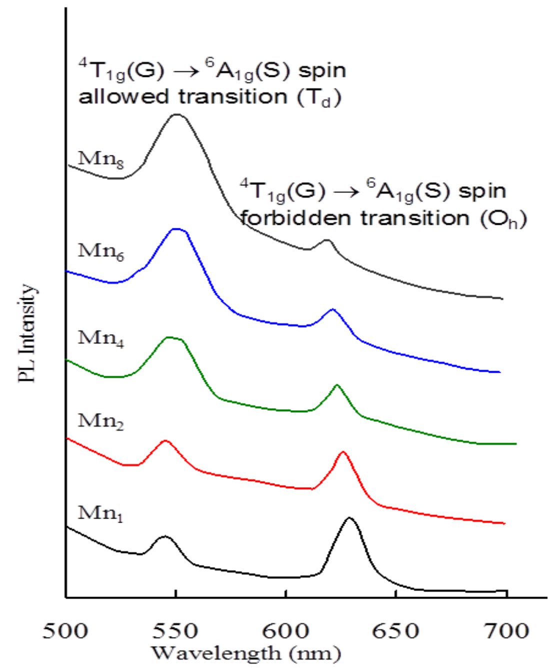

Fig. 3: Photoluminescence spectra of LiI-AgI-B_2O_3 glasses doped with different concentrations of MnO recorded at room temperature.

Thus the summary of the results of spectroscopic studies is as follows: the manganese ions do exist in both Mn^{2+} and Mn^{3+} states in LiI–AgI– B_2O_3 glass network. Mn^{2+} ions occupy both octahedral and tetrahedral positions in the glass network. With the increase in the concentration of MnO in the glass network, there is a gradual increase in the tetrahedral occupancy of Mn^{2+} ions at the expense of octahedral occupancy.

Conclusions:

- LiI–AgI– B_2O_3 glasses mixed with different concentrations of MnO (ranging from 0 to 0.8 mol%) were synthesized.
- A variety of properties viz., electrical, dielectric and spectroscopic properties that include optical absorption, ESR, and photoluminescence studies have been investigated.
- The differential thermal analysis of these samples has indicated an increase in thermal stability of glass against devitrification with increase in the concentration of MnO.
- The optical absorption and ESR studies indicated that a part of manganese ions do exist in Mn^{2+} and Mn^{3+} state in these samples.
- The results of these studies along with luminescence spectral results have indicated that as the concentration of MnO increased there is gradual transformation of Mn^{2+} ions from octahedral to tetrahedral positions in the glass network.

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