

Optical Properties of Mn²⁺ Doped Lead Phosphate (Lp) Glasses

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Received 2012

ABSTRACT

Doping of MnO (less than One mole %) in LP glass system promotes the transparency and the general quality of the LP glass.- Mn²⁺ occupying an O_h site in the LP glass network - The influence of the LP glass network on Mn²⁺ energy levels and its electronic structure seems to be different when the concentration of MnO is extremely small (0.2 mole%) - The observation of single band of Mn²⁺ in this case probably correlates well with the observation of forbidden hyperfine EPR transitions in the same glass.

Keywords: Lead Phosphate; Optical Absorption Spectra; Ligand Coordination; Eutectic Mixture; Crystal Field Environment; Forbidden Bands

1. Introduction

In this article the optical investigations made on [x (PbO - (1-x) P₂O₅)] Lead Phosphate (LP) glasses and were discussed. The objective of studying optical absorption spectra of Mn²⁺ doped LP glass system is two fold. Firstly it is interesting to understand the effect of magnetic ion like Mn²⁺ on the absorption edge in particular and on energy bands in general of LP glass system. Secondly it is much more interesting to study the effect of lead phosphate glass network on the electronic structure and energy levels of Mn²⁺ ion.

The energy level diagram of Mn²⁺ is same in O_h and T_d, the spectra in the two geometry's are distinct which is the most interesting [1] aspect of the optical study.

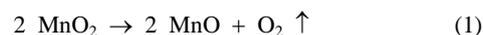
There appear to be not many investigations on the electronic absorption spectra of Mn²⁺ ion in glasses [1] probably for weak and poorly, resolved optical absorption bands in glasses. However, there are some reports on optical absorption spectra of Mn²⁺ doped silicate, [1-3] borate [1-2] phosphate [1-6] and other glasses. As already mentioned, although Mn²⁺ can enter into O_h or T_d site in a glass, the absorption spectra observable could be different depending on various factors.

However, optical absorption bands of Mn²⁺ are still expected to appear in greater intensity if Mn²⁺ exists in T_d - ligand coordination than when it exists in O_h - ligand coordination. Thus, "Mn²⁺ is an excellent ion for probing the local site geometry in various glassy matrices even by optical absorption technique", even though its overall absorptivity is very low. Because of the number and energy distribution of distinct ligand field - sensitive transitions observable, the potential value of Mn²⁺ for structural diagnosis studies in glasses is very high, but so far it has not been fully exploited. The present work aims at filling up this gap to a certain extent.

2. Experimental

The Mn²⁺ doped LP glasses were prepared by taking PbO, ADP

and suitable quantity of MnO₂ together and thoroughly mixing and grinding the chemicals. Thus, the method of preparation of the Mn²⁺ doped LP glasses is exactly same as describe in the [7]. However, certain observations in respect of liquidus temperature and the time required for the melt to be maintained at that temperature have been made. Since MnO₂ in the eutectic mixture of PbO and P₂O₅ is expected to undergo the chemical reaction.



It is observed that effervescence takes place at the melt temperature. Therefore, the time required to obtain clear, transparent and bubble free melt was longer in the case of MnO doped LP glasses. These observations indicate that the presence of MnO as an impurity promotes the ease with which the glasses can be prepared. Further, the glasses obtained were less hygroscopic, chemically more durable with better homogeneity and visibly more transparent than their corresponding undoped LP glasses. These doped glasses were used for recording the optical absorption spectra, sometimes, in conjunction with the undoped glasses.

3. Results and Discussion

The optical absorption spectra in the range of 200 to 700 nm typically for Mn²⁺ doped LP glasses with x = 0.35, 0.40, 0.45 containing higher concentration (0.7 mole%) of Mn²⁺ are shown in **Figure 1** as curves A, B, C, respectively. For x = 0.50, the spectrum is shown as curve D in **Figure 2** respectively. It is seen in all these spectra that both visible and UV regions are totally free from any absorption bands due to Mn²⁺. At the same time it is seen that, the absorption edges of these doped glasses are almost unaffected within the error of ± 2 nm.

Specifically, in **Figure 2** the spectra of undoped and Mn²⁺ doped glasses (x = 0.5) are given together for comparison. While the optical absorption edge at 258 ± 2 nm coincides for both the glasses, it can be seen that the absorbance of undoped

glass is higher than the absorbance of the Mn^{2+} doped glass. In order to make proper comparison of the transparency of the undoped and Mn^{2+} doped (high concentration, (HC)) glasses, the absorption coefficients of these glasses have been calculated at the average wavelength (550 nm) of the visible region. The values are found to be

$$\alpha = 10.7 \text{ cm}^{-1} \text{ (undoped), } \alpha = 1.6 \text{ cm}^{-1} \text{ (Mn}^{2+} \text{ doped)}$$

These values clearly suggest that Mn^{2+} doped glasses are at least 7 times [i.e. ratio of α (undoped) to α (doped)] more transparent than the undoped glasses. Thus the role of Mn^{2+} impurity in LP glass appear to be limited to promoting the ease of glass formation, while having no effect on the absorption edge. This appears to be due to the small concentration of Mn^{2+} impurity in the glass.

It is surprising that the Mn^{2+} in any of $x \text{ PbO} - (1-x) \text{ P}_2\text{O}_5$ glasses does not exhibit any d-d bands.

The Mn^{2+} ion (d^5) has five unpaired electrons in the valence shell distributed in the t_{2g} and e_g orbitals either in O_h or T_d symmetry. In free ion state it will give rise to a number of free ion terms in the increasing order of energy $6S, 4G, 4P, 4D, 2I, 2G, 2H, 4F, 2D, 2F, 2F, 2S, 2D, 2G, 2P$ and $2D$. When the ion is placed in a ligand field, these levels split further into number of components depending on the strength of crystal field environment [4,6]. The energy level diagram for d^5 configuration has been

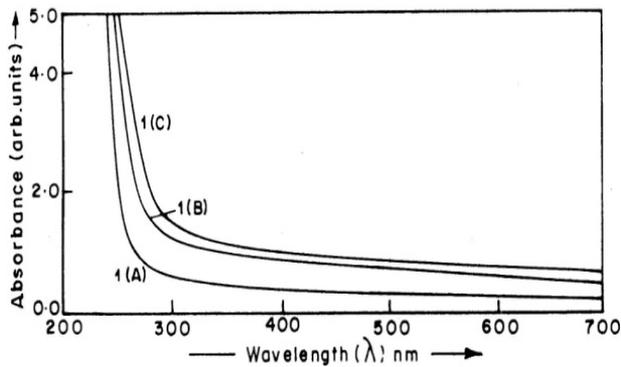


Figure 1. Optical absorption spectra of Mn^{2+} doped (HC) (LP) glasses. 1(A) 0.35 PbO-0.65 P_2O_5 , 1(B) 0.40 PbO-0.60 P_2O_5 , 1(C) 0.45PbO-0.55 P_2O_5 .

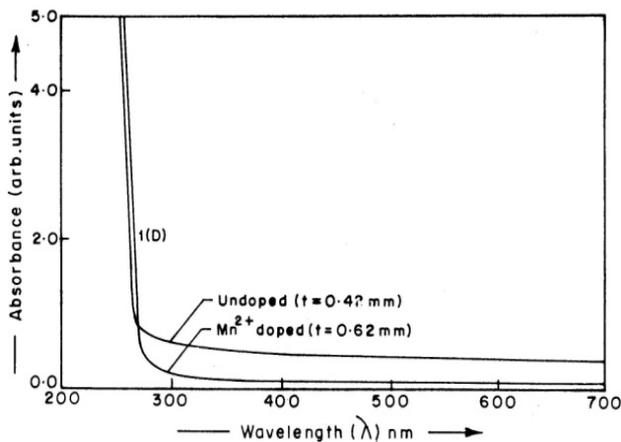


Figure 2. Optical absorption Spectra of undoped and Mn^{2+} doped $0.50P_2O_5$ glass.

$Mn^{2+}(d^5)$ they have been discussed in the literature extensively. Since not a single band in the Mn^{2+} (HC) doped LP glass has been calculated by number of authors including Tanabe and Sugano [8] and Orgel [9]. Tanabe and Sugano or Orgel diagram for been observed, it is felt that either concentration of Mn^{2+} is not sufficient or lead phosphate glass system as such has great influence on the absorption bands of Mn^{2+} ion. One fact that can be concluded with certainty is that the Mn^{2+} in LP glass system occupies an O_h site in which case the absorption bands are expected to be very weak. On the other hand if Mn^{2+} ion were to be in a T_d ligand coordination mixing of d-orbitals with p-orbitals is expected to take place [2]. As a result, the absorption intensity is expected to be 10 to 100 times more than that due to the ion in the O_h environment.

Our efforts to increase the concentration of Mn^{2+} in the LP glasses by the addition of higher quantities of starting chemical, MnO_2 have not been successful. With increase in the concentration of MnO_2 , the lead phosphate glasses are found to gain color but no specific bands of Mn^{2+} could be observed. This indicates that higher amount of MnO_2 does not lead to higher number of Mn^{2+} ions and probably Manganese changes to other oxidation states of Mn^{3+} , Mn^{6+} or even Mn^{7+} . Therefore, for increasing Mn^{2+} ions, the starting compound may have to be different from MnO_2 .

Figure 3 gives the absorption spectra of both undoped and doped (low concentration, (LC)) LP glass for $x = 0.5$.

The absorption coefficients calculated for undoped and doped glasses are $\alpha = 7.6 \text{ cm}^{-1}$ (undoped) $\alpha = 4.3 \text{ cm}^{-1}$ (Mn^{2+} doped), which suggest that doped glass is again more transparent (1.8 times).

In order to detect the presence of any weak absorption bands due to Mn^{2+} in this particular LP glass (**Figure 3**). The absorption spectrum of doped glass has been recorded with the undoped glass in the path of the reference beam to compensate for the host network absorption. It is interesting to note that the effort led to the detection of a weak but definite absorption band at 261 nm ($38,310 \text{ cm}^{-1}$) shown in **Figure 4**. A comparison of the peak position of this band with the bands reported in the literature [4] indicates that it should be attributed to $6A_{1g} \rightarrow 4A_{2g}$ (F) transition. This observation seems to be peculiar for LP glass with $x = 0.5$ containing low concentration (LC) of Mn^{2+} .

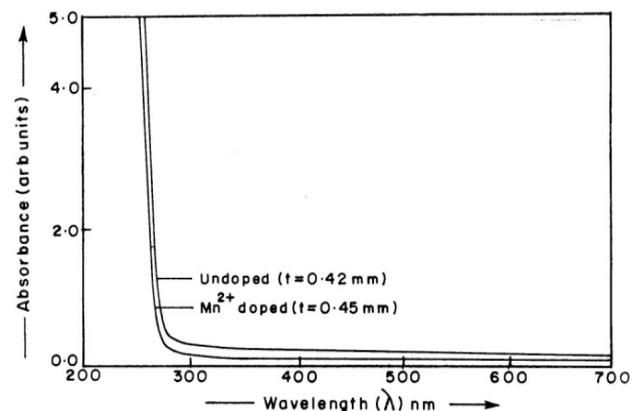


Figure 3. Optical absorption spectra of undoped and Mn^{2+} doped (LC) $0.50PbO-0.50P_2O_5$ (LP) glass.

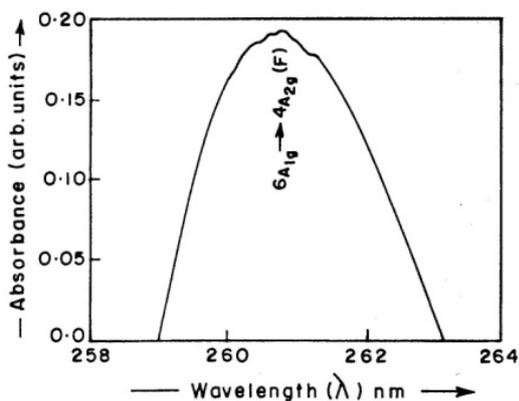


Figure 4. Optical absorption spectrum of Mn^{2+} ion in 0.50PbO-0.50P₂O₅ glass.

4. Conclusions

The results clearly suggest that MnO in concentrations less than one mole % has no significant effect on the absorption edge or energy bands of lead phosphate glass system. However, it definitely promotes the transparency and the general quality of the LP glass formation.

The effect of lead phosphate system on the energy levels of Mn^{2+} seems to be such that the absorptivity of the forbidden bands of Mn^{2+} is extremely low or zero. Clearly this is due to Mn^{2+} occupying an O_h site in the glass network.

The influence of the LP glass network on Mn^{2+} energy levels and its electronic structure seems to be different when the concentration of MnO is extremely small (0.2 mole%). The observation of single band of Mn^{2+} in this case probably correlates well with the observation of forbidden hyperfine EPR transitions in the same glass.

5. Acknowledgements

I express my sincere thanks to university grants commission (UGC), New Delhi, India for the encouragement and financial assistance to Minor Research Project "Structural Investigation of Low Melting Glass Systems". I am thankful to Prof. M. Salagram, for his guidance and suggestions. I am also thankful to Sri Rajesh C Shah, Correspondent, Prof. T.V.Rao, Principal, Pragati Mahavidyalaya Degree College, Gujarati Pragati Samaj for their help and constant support. I also express my sincere thanks to Sri K. Vidya Sagar Rao, Chairman, M. Narashimulu, Secretary, Dr. Parameshwar Reddy, Academic Director, A. Mahesh Babu, Executive Director, and Dr. Dargaiah, Principal Tirumala Engineering College, Hyderabad, India for their help, encouragement and constant support.

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