

SPECTROSCOPIC STUDIES OF PbO-Sc₂O₃-P₂O₅ GLASSES WITH MoO₃

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ABSTRACT:

PbO-Sc₂O₃-P₂O₅ glasses containing different concentrations of MoO₃ ranging from 0 to 0.5 mol% were prepared. Spectroscopic studies viz., infrared and ESR spectra of these glasses have been carried out as a function of molybdenum ion concentration. The analysis suggests that the molybdenum ions exist in Mo⁵⁺ state with Mo(V)O³⁻ complexes that act as modifiers in addition to Mo⁶⁺ state with MoO₄ and MoO₆ structural groups in these glasses.

Keywords: Lead, Scandium, phosphate glasses, Molybdenum ion, infrared spectra and ESR spectra.

1. INTRODUCTION

Phosphate based glasses are both scientifically and technologically important materials because they generally offer some unique physical properties better than other glasses because of the linked PO₄ structural units with covalent bonding in chains or rings by bridging oxygen's [1-4]. These glasses have poor chemical durability that often limits their usefulness that can be improved by the substitution of various oxides such as lead oxide [5,6], have low melting and glass transition temperature [7,8], high electrical conductivity [9], high thermal expansion coefficient [10], and high ultraviolet (UV) transmission [11,12]. These properties making them useful candidates for fast ion

conducting materials [13], laser host matrices after doping with rare-earth elements [14,15], glass-to-metal seals [16], and for the immobilization and disposal of nuclear waste were reported [17,18].

Investigations of lead phosphate glasses have revealed that the modifier/former role of PbO depends on PbO concentration in the glass composition 40 PbO-(10-x) Sc₂O₃-50P₂O₅-x MoO₃ with 0 ≤ x ≤ 0.5 mol%. The created P-O-Pb bonds along with the high ionic field strength and polarizability of Pb²⁺ ions control the physical properties of lead phosphate glasses. Depending on the studied glass system, the Pb²⁺ ions show an intermediate character between former and modifier. As a glass former, PbO enters the network with PbO⁴ structural units by sharing the corners of phosphate network which in turn form P-O-Pb linkages. When PbO acts as network modifier, Pb is octahedrally coordinated and behaves like any other conventional alkali oxide modifier [19, 20].

Scandium oxide (Sc₂O₃), among the high-index materials in the ultraviolet ~UV! spectral range is a promising material for laser optical coatings, due to its relatively high damage threshold. [21–26].

On the other hand, there has been an enormous amount of researches on improving the physical properties of phosphate glasses that make them potential materials for electro-optical applications by introducing a number of transition metal oxides like MoO_3 , Ag_2O or PbO to form binary or ternary glass systems. It was revealed that, molybdenum-phosphate glasses belong to a group of glasses which incorporate distorted octahedral structural units $[\text{MoO}_6]$ or tetrahedral structural units $[\text{MoO}_4]$ within the glass network [27-32]. Molybdenum oxide combined with P_2O_5 forms binary glasses over wide and continuous compositional range [33]. The molybdenum ions exist in at least two stable valence states as Mo^{5+} and Mo^{6+} in the glass network depending upon the chemical composition of the host network. The Mo^{6+} ions participate in the network forming, whereas Mo^{5+} ions act as modifiers. Earlier ESR studies on the glass systems containing molybdenum ions have predicted that Mo^{5+} ions are present in octahedral coordination along with distorted octahedrons approaching tetragons. Further, Mo-O bond in molybdenum hexavalent oxide is identified as significantly covalent [34, 35]. A considerable number of recent studies on various physical properties viz., spectroscopic, d.c conductivity, dielectric properties, etc., of variety of glass systems containing molybdenum ions are available in the literature [36-41].

The objective of this paper is to have a comprehensive understanding over the topology and valence states of molybdenum ions in $\text{PbO}-\text{Sc}_2\text{O}_3-\text{P}_2\text{O}_5$ glass system, by a systematic study of ESR spectra coupled with IR spectra.

2. EXPERIMENTAL

For the present study a particular composition viz., $40\text{PbO}-(10-x)\text{Sc}_2\text{O}_3-50\text{P}_2\text{O}_5: x\text{MoO}_3$ with $x = 0$ (PSPM₀), 0.1 (PSPM₁), 0.2 (PSPM₂), 0.3 (PSPM₃), 0.4 (PSPM₄) and 0.5 (PSPM₅) all by mol %, has been chosen.

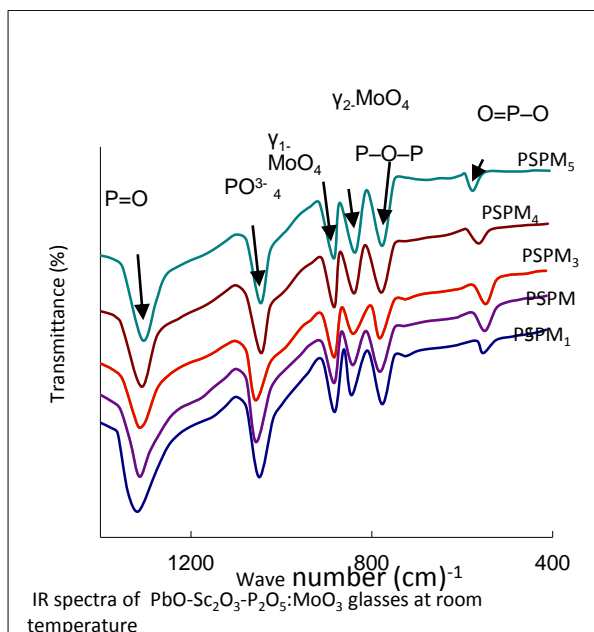
The materials were $(\text{NH}_4)_2\text{HPO}_4$, PbO , Sc_2O_3 , and MoO_3 of reagent grade purity. The samples were prepared by weighing suitable proportions of the components; the powder was mixed thoroughly in an agate mortar and melted in a thick-walled platinum crucible between $1000^\circ\text{C}-1200^\circ\text{C}$ in an automatic temperature controlled furnace for about 1h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed from 300°C with a cooling rate of $1^\circ\text{C}/\text{min}$. The samples were then ground and optically polished. The final dimensions of the samples used optical studies were about $1\text{cm} \times 1\text{cm} \times 0.2\text{cm}$. The density 'd' of the glasses was determined to an accuracy of 0.001 by standard principle of Archimedes using o-xylene (99.99% pure) as the buoyant liquid.

The ESR spectra of the fine powders of the samples were recorded at room temperature on E11Z Varian X-band ($\gamma = 9.5\text{GHz}$) ESR spectrometer. Infrared transmission spectra were recorded on a Bruker IFS 66V-IR spectrometer with resolution of 0.1cm^{-1} in the range $400-2000\text{cm}^{-1}$ using potassium bromide pellets (300mg) containing powder form of the glass (1.5mg).

3. RESULTS

The infrared transmission spectra of $\text{PbO}-\text{Ga}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses exhibit vibrational bands at about 1315cm^{-1} (identified due to P=O stretching vibration, this region may

also consist of bands due to anti-symmetrical vibrations of PO_4^{3-} groups), 1050 cm^{-1} (a normal vibrational mode in PO_4^{3-} group arising out of γ_3 -symmetric stretching), at 777 cm^{-1} (due to P-O-P symmetric bending vibrations) and another band at 554 cm^{-1} due to O=P-O vibrations [42,43]. Two bands have also located at 882 and 840 cm^{-1} in the spectrum, these bands are identified due to γ_1 (symmetric stretching vibrations) and γ_2 (doubly degenerate stretching vibrations) vibrational modes of MoO_4 groups [40] that take part in the glass network forming positions.

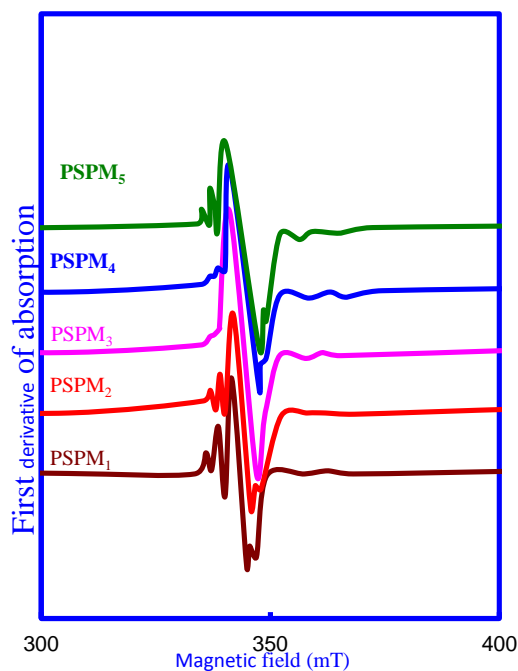


With the increase of MoO_3 , the intensity of bands due to P=O, PO_4^{3-} , P-O-P are observed to decrease up to 0.3 mole% of MoO_3 beyond that concentration a reverse trend is observed. A summary of the data for the positions of various bands in the IR spectra of the $PbO-Sc_2O_3-P_2O_5$ glasses doped with different concentrations of MoO_3 is presented.

Summary of data for positions (cm^{-1}) of various absorption bands in the IR spectra of $PbO-Sc_2O_3-P_2O_5: MoO_3$ glasses.

Band	PSP M ₁	PSP M ₂	PSP M ₃	PSP M ₄	PSP M ₅
P=O-P	554	550	548	564	577
PO_4^{3-}	104	105	105	105	104
groups	9	6	7	0	7
P-O-P symmetric stretching	777	782	786	779	774
P=O stretching	131	131	131	131	131
$\nu_1 - MoO_4$	882	882	882	880	871
$\nu_3 - MoO_4$	845	847	849	839	837

The ESR spectra, recorded at room temperature for $PbO-Sc_2O_3-P_2O_5:MoO_3$ glasses under investigation the spectra exhibit a central line surrounded by smaller satellites with $g_{\perp} = 1.945$ and $g_{\parallel} = 1.889$ due to paramagnetic Mo^{5+} ion. They may be attributed to the ^{95}Mo (15.7%) and ^{97}Mo (9.4%) isotopes which have the nuclear spin $I = 5/2$. The intense central line belongs to the ^{96}Mo isotope which has the nuclear spin $I=0$. The intensity is found to increase with increase in the concentration of MoO_3 up to 0.3 mol % and after that the intensity is found to decrease.



ESR spectra of PbO–Sc₂O₃–P₂O₅:MoO₃ glasses recorded at room temperature. Inset shows the variation of intensity of the signal with

4. DISCUSSION

P₂O₅ is a well-known strong glass forming oxide, Participates in the glass network with PO₄ structural units. One of the four oxygen atoms in PO₄ tetrahedron is doubly bonded to the phosphorous atom with the substantial π -bond character to account for pentavalency of phosphorous. The PO₄ tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each PO₄ tetrahedron, in general, the P-O-P bond between PO₄ tetrahedra is much stronger than the cross bond between chains via the metal cations [44].

PbO in general is a glass modifier and enters the glass network by breaking up the P-O-P (normally the oxygens of PbO break the local symmetry while Pb²⁺ ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non bridging

ions. In this case the lead ions are octahedrally positioned. To form octahedral units, Pb should be sp³d² hybridized (6s, 6p and 6d orbitals) [45,46]. However, Bo may also participate in the glass network with PbO₄ structural units when lead ion is linked to four oxygens in a coalency bond configuration. In such a case the network structure is considered to built up from PbO₄ and PO₄ pyramidal units, with P-O-Pb linkages.

Molybdenum ions are expected to exist mainly in Mo⁶⁺ state in the present PbO–Sc₂O₃–P₂O₅ glass network. These Mo⁶⁺ ions are expected to participate in the glass network with tetrahedral MoO₄²⁻ structural units. However, regardless of the oxidation state of the molybdenum ion in the starting glass batch, the final glass contains both Mo⁶⁺ and Mo⁵⁺. When MoO₃ enters as modifier in the glass network, the π -bond of P=O may be ruptured with the creation of new non-bridging oxygen ions; the observed gradual decrease in the intensity of the band due to P=O stretching vibrations with an increase in the concentration of MoO₃ up to 0.3 mol% clearly suggests the increasing modifying action of MoO₃. The decrease in the intensities of the bands due to P–O–P symmetric stretching vibrations and the simultaneous increase in intensity of the band due to P–O–P asymmetric bending vibrations also lead to a similar conclusion. The band due to ν_1 vibrational mode of MoO₄²⁻ tetrahedral units located at about 882 cm⁻¹ is observed to be shifted towards a region of higher wave number; in this region the band due to partially isolated Mo-O bonds of the strongly deformed MoO₆ groups is expected [48]. Similarly the ν_2 vibrational band of MoO₄²⁻ units observed at about 840 cm⁻¹ in the spectra is shifted towards on the region of

asymmetric stretching vibrations of Mo_{short}O_{long}-Mo bridge associated with MoO₆ octahedra containing Mo=O bond [47]. These results confirm a gradual transformation of molybdenum ions from tetrahedral octahedral positions to octahedral positions with increase in the concentration of MoO₃ up to 0.3 mol%. Beyond that range of MoO₃, there is a growing concentration of molybdenum ions that take part in network forming positions with MoO₄²⁻ tetrahedral units.

The highest intensity of the signal observed in the ESR spectrum of the glass PSPM₃ suggests the presence of the highest concentration of Mo⁵⁺O³⁻ complexes. The values of g_⊥ and g_∥ from this spectrum have been found to be dependent on the concentration of the MoO₃; the structural disorder arising from the site-to-site fluctuations of the local surroundings of the paramagnetic Mo⁵⁺ ions can be accounted for such variations. The variation of MoO₃ content has considerably affected the intensity of the signal; in fact, the signal is observed to be feeble for the samples with lower concentration of MoO₃ and higher than 0.3 mole % of MoO₃.

Summing up the discussion, there is a maximum concentration of molybdenum ions that are present largely in Mo⁵⁺ state, adopt modifying positions and create bonding defects when the concentration of MoO₃ is around 0.3 mol% in the glass network. After that the increase of MoO₃ caused an enhancement in the concentration of Mo⁶⁺ ions that take part network forming positions with tetrahedral MoO₄²⁻ structural units.

5. CONCLUSIONS

The summary of the conclusions drawn from various studies of PbO-Sc₂O₃-P₂O₅ glass doped with MoO₃ is as follows: ESR spectral studies also indicated a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO₃ up to 0.3mol% and beyond that concentration an enhancement in the concentration of Mo⁶⁺ ions that take part network forming positions with tetrahedral MoO₄²⁻ structural units. The IR Spectral studies indicate that the molybdenum ions occupy octahedral positions in larger concentrations in PSPM₃.

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