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I R Spectra of Lead Gallium Phosphate Glasses Doped With Molybdenum Ions

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Abstract— **$PbO-Ga_2O_3-P_2O_5$ glasses containing small concentrations of MoO_3 (ranging from 0 to 0.5mol%) were prepared. IR Studies of these glasses were carried out. The studies indicate that the molybdenum ions occupy octahedral positions in larger concentrations in M_5.**

Index Terms—**Lead, Gallium,Phosphate glasse, molybdenum ions,IR studies.**

I. INTRODUCTION

Phosphate based glasses are both scientifically and technologically important materials because they commonly put forward some unique physical properties better than other glasses because the bridging oxygen's linked PO_4 structural units with covalent bonding in chains or rings [1].These glasses contain poor chemical durability that often limits their usefulness that can be enhanced by the substitution of various oxides such as lead oxide [2],have low melting and glass transition temperature [3],high electrical conductivity, high thermal expansion coefficient, and high ultraviolet (UV) transmission [4]. These properties making them useful candidates for fast ion conducting materials, laser host matrices after doping with rare-earth elements , glass-to-metal seals , and for the immobilization and disposal of nuclear waste were reported [5].

Investigations of lead phosphate glasses have revealed that the modifier/former role of PbO depends on PbO concentration in the glass composition 45 $PbO-(5-x)Ga_2O_3-50P_2O_5-x\ MoO_3$ with $0 \leq x \leq 0.5$ mol%. The formed P-O-Pb bonds along with the high ionic field strength and polarizability of Pb^{2+} ions organize the physical properties of lead phosphate glasses. Depending on the studied glass system, the Pb^{2+} ions show an transitional character between former and modifier. As a glass former, PbO enters the network with PbO^4 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 [6].

Ga_2O_3 is a heavy metal oxide and when it is introduced in the glass matrix it may influence the physical properties, i.e. refractive index, thermal expansion coefficient, chemical resistance, glass transition temperature and infrared transmittance. This can make the glasses suitable for use as infrared windows, ultra fast optical switches, optical isolators and other photonic devices for communication and advanced computer applications. Many recent investigations on the role of Ga_2O_3 in various glass matrices including some phosphate glasses have been published .

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 [MoO_6] or tetrahedral structural units [MoO_4] within the glass network . Molybdenum oxide combined with P_2O_5 forms binary glasses over wide and continuous compositional range .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. 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 [7].

Therefore, the objective of the present study is to investigate the structural influence of MoO_3 on the lead phosphate glasses doped with Ga_2O_3 through a detailed investigation on IR.

II. EXPERIMENTAL METHODS

Within the glass forming region of $PbO-Ga_2O_3-P_2O_5$ glass system, a particular composition $45PbO-(5-x)\ Ga_2O_3-50P_2O_5$: x MoO_3 (with x ranging from 0 to 0.5) is chosen for the present study. The details of the composition are:

M_0:$45PbO-5Ga_2O_3-50P_2O_5$
M_0:$45PbO-4.9Ga_2O_3-50P_2O_5$:$0.1MoO_3$
M_0:$45PbO-4.8Ga_2O_3-50P_2O_5$:$0.2MoO_3$
M_0:$45PbO-4.7Ga_2O_3-50P_2O_5$:$0.3MoO_3$
M_0:$45PbO-4.6Ga_2O_3-50P_2O_5$:$0.4MoO_3$
M_0:$45PbO-4.5Ga_2O_3-50P_2O_5$:$0.5MoO_3$

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 at 1150°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

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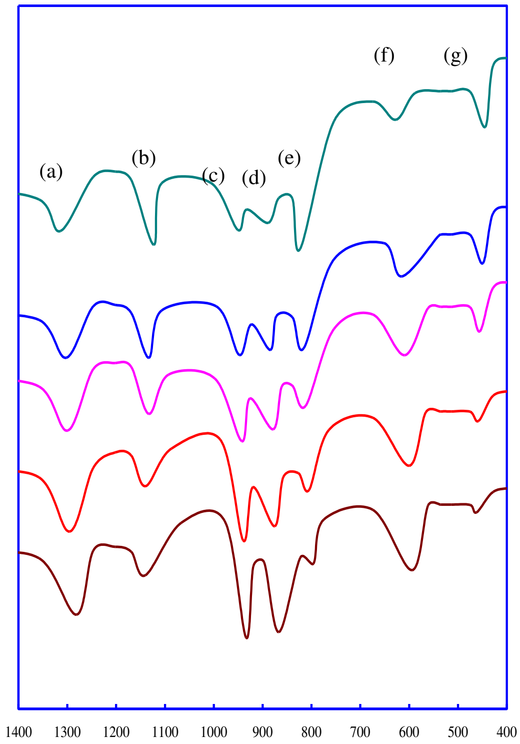
subsequently annealed from 300°C with a cooling rate of 1°C/min. Infrared transmission spectra were recorded on a Bruker IFS 66V-IR spectrometer with resolution of 0.1 cm^{-1} in the range 400-2000cm^{-1} using potassium bromide pellets (300mg) containing powder form of the glass (1.5mg).

III. RESULTS

Fig. 1 shows the effect of MoO_3 on the infrared spectra of the PbO-Ga_2O_3-P_2O_5 glasses. The infrared spectra of the studied glasses showed some different frequency regions. The bands located at around 509 – 526 cm^{-1} are assigned to the bending vibrations of PO^-_2 groups[8]. Additionally, the spectrum of each glass exhibits a weak band at about 615 cm^{-1}, identified as due to the vibrations of GaO_4 units [9]. The bands at around 755-778 cm^{-1} are assigned to symmetric stretching vibrations of P-O-P rings [10]. Two bands have also located at 890 and 830 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 [11] that take part in the glass network forming positions. The bands at around 907-930 cm^{-1} are related to P-O-P asymmetric stretching vibrations of bridging oxygen atoms in P-O-P bands .The band at around 1042 cm^{-1} which is attributed to vibrations of PO_4^{3-} groups .The vibrational bands around 1260 cm^{-1} are attributed to symmetric stretching mode of P=O [12].



(a) symmetric stretching mode of P=O bond (b)
P-O-P asymmetric
(c) PO43- groups (d) P-O-P symmetric
stretching/MoO4 specific
vibrations (e) MoO6 specific vibrations (f) GaO4
units (g)Pb-O Units

IV. DISCUSSION

P_2O_5 is a well-known strong glass forming oxide, Participates in the glass network with PO_4 structural units. One of the four oxygen atoms in PO_4 tetrahedron is doubly bonded to the phosphorous atom with the substantial π-bond character to account for pentavalency of phosphorous. The PO_4 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 PO_4 tetrhedron;in general, the P-O-P bond between PO_4 tetrahedra is much stronger than the cross bond between chains via the metal cations [13].

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 Pb^{2+} 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 sp^3d^2 hybridized (6s,6p and 6d orbitals)[14,15].However, Pbo may also participate in the glass network with PbO_4 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 PbO_4 and PO_4 pyramidal units, with P-O-Pb linkages. Molybdenum ions are expected to exist mainly in the Mo^{6+} state in the present PbO-Ga_2O_3-P_2O_5 glass network. However, the reduction of Mo^{6+} state to the Mo^{5+} state is viable during melting and subsequent annealing process. These Mo^{5+} ions are quite stable and occupy octahedral positions with distortions due to the Jhon-Teller effect [16, 17]. The IR analysis of binary PbO-P_2O_5 glasses the existence of PO_4 joined by one P-O-P bonds. Addition of PbO depolymerize a number of phosphorous-oxygens chains by forming new P-O-Pb bonds and non bridging oxygens in the glass network, and Pb^{2+} ions will occupy positions between P-O-P layers by forming ionic bonding. The intensity of bands due to PO_2^- groups and PO_4^{3-} groups are observed to grow at the expense of symmetric stretching P=O bonds and P-O-P rings. The band due to υ_1 vibrational mode of MoO_4^{2-} tetrahedral units located at about 890 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 MoO_6 groups is expected. Similarly the υ_3 vibrational band of MoO_4^{2-} units observed at about 830 cm^{-1} in the spectra is shifted towards on the region of antisymmetric stretching vibrations of $Mo\text{-}_{short}O_{long}\text{-}Mo$ bridge associated with MoO_6 octahedra containing Mo=O bond. These results confirm a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO_3.

V. CONCLUSION

The IR Spectral studies indicate that the molybdenum ions occupy octahedral positions in larger concentrations in M_5.

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