

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

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Abstract— PbO-Ga₂O₃-P₂O₅ glasses containing small concentrations of MoO₃ (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 M₅.

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 PO₄ 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)Ga₂O₃-50P₂O₅-x MoO₃ with 0 ≤ x ≤0.5 mol%. The formed P-O-Pb bonds along with the high ionic field strength and polarizability of Pb²⁺ ions organize the physical properties of lead phosphate glasses. Depending on the studied glass system, the Pb²⁺ ions show an transitional 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 [6].

Ga₂O₃ 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 Ga₂O₃ 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 MoO₃,Ag₂O 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 [MoO₆] or tetrahedral structural units [MoO₄] within the glass network . Molybdenum oxide combined with P₂O₅ forms binary glasses over wide and continuous compositional range .The molybdenum ions exist in at least two stable valence states as Mo⁵⁺ and Mo⁶⁺ in the glass network depending upon the chemical composition of the host network. The Mo⁶⁺ ions participate in the network forming, whereas Mo⁵⁺ ions act as modifiers. Earlier ESR studies on the glass systems containing molybdenum ions have predicted that Mo⁵⁺ 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 MoO₃ on the lead phosphate glasses doped with Ga₂O₃ through a detailed investigation on IR.

II. EXPERIMENTAL METHODS

Within the glass forming region of PbO-Ga₂O₃-P₂O₅ glass system, a particular composition 45PbO-(5-x) Ga₂O₃-50P₂O₅ : x MoO₃ (with x ranging from 0 to 0.5) is chosen for the present study. The details of the composition are:

M₀:45PbO-5Ga₂O₃-50P₂O₅

M₀:45PbO-4.9Ga₂O₃-50P₂O₅:0.1MoO₃

M₀:45PbO-4.8Ga₂O₃-50P₂O₅:0.2MoO₃

M₀:45PbO-4.7Ga₂O₃-50P₂O₅:0.3MoO₃

M₀:45PbO-4.6Ga₂O₃-50P₂O₅:0.4MoO₃

M₀:45PbO-4.5Ga₂O₃-50P₂O₅:0.5MoO₃

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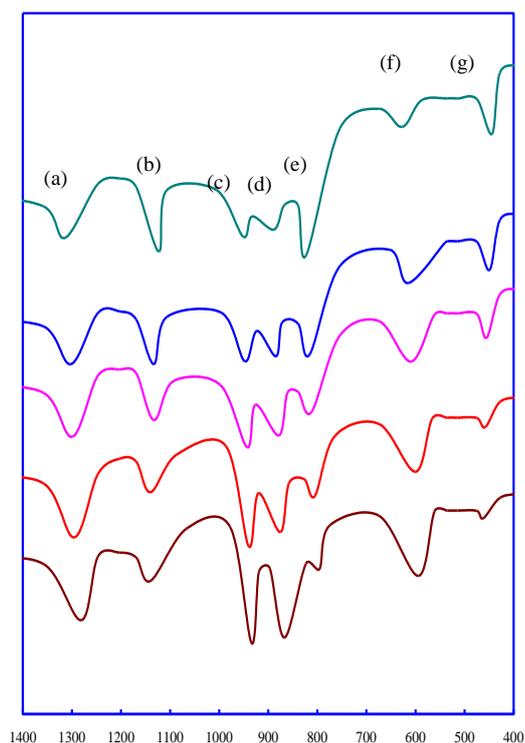
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subsequently annealed from 300°C with a cooling rate of 1°C/min. Infrared transmission spectra were recorded on a Bruker IFS 66V-IR spectrometer with resolution of 0.1 cm⁻¹ in the range 400-2000cm⁻¹ using potassium bromide pellets (300mg) containing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

III. RESULTS

Fig. 1 shows the effect of MoO₃ on the infrared spectra of the PbO-Ga₂O₃-P₂O₅ 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 PO₂ groups[8]. Additionally, the spectrum of each glass exhibits a weak band at about 615 cm⁻¹, identified as due to the vibrations of GaO₄ 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 MoO₄ 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 PO₄³⁻ 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

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 [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 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)[14,15]. However, PbO 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 the Mo⁶⁺ state in the present PbO-Ga₂O₃-P₂O₅ glass network. However, the reduction of Mo⁶⁺ state to the Mo⁵⁺ state is viable during melting and subsequent annealing process. These Mo⁵⁺ ions are quite stable and occupy octahedral positions with distortions due to the Jhon-Teller effect [16, 17]. The IR analysis of binary PbO-P₂O₅ glasses the existence of PO₄ 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 Pb²⁺ ions will occupy positions between P-O-P layers by forming ionic bonding. The intensity of bands due to PO₂⁻ groups and PO₄³⁻ groups are observed to grow at the expense of symmetric stretching P=O bonds and P-O-P rings. The band due to ν_1 vibrational mode of MoO₄²⁻ 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 MoO₆ groups is expected. Similarly the ν_3 vibrational band of MoO₄²⁻ units observed at about 830 cm⁻¹ in the spectra is shifted towards on the region of antisymmetric stretching vibrations of Mo-short O_{long}-Mo bridge associated with MoO₆ 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 MoO₃.

V. cONCLUSION

The IR Spectral studies indicate that the molybdenum ions occupy octahedral positions in larger concentrations in M₅.

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