



E S R Spectra of PbO-Ga₂O₃-P₂O₅:MoO₃ Glasses

Dr.B.Lakshmanarao

Lecturer in Physics, Avanigadda Government Degree College,Avanigadda,Krishna District, A.P, India

K.Jyothi Raju

Research Scholar,Krishna University, Machilipatnam,Krishna District, A.P, India

Dr.S.V.G.V.A.Prasad

Lecturer in Physics,Ideal College of Arts And Sciences(A), Kakinada,E.GDistrict, A.P, India

EMAIL: somarouthu13@Yahoo.co.in

Abstract

Abstract: PbO-Ga₂O₃-P₂O₅ glasses containing small concentrations of MoO₃ (ranging from 0 to 0.5mol%) were prepared. ESR Studies of these glasses were carried out. The studies indicate that the molybdenum ions occupy octahedral positions in larger concentrations inPGPM₅.

Key Words:

Lead Glasses; Phosphate Glasses; Molybdenum; ESR studies

1.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 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 can be used for revealing the structural details of these glasses since these are very sensitive to the local symmetry, the character of the chemical bond and other structural properties

2.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:

PGPM₀:45PbO-5Ga₂O₃-50P₂O₅

PGPM₀:45PbO-4.9Ga₂O₃-50P₂O₅ :0.1MoO₃

PGPM₀:45PbO-4.8Ga₂O₃-50P₂O₅:0.2MoO₃

PGPM₀:45PbO-4.7Ga₂O₃-50P₂O₅:0.3MoO₃

PGPM₀:45PbO-4.6Ga₂O₃-50P₂O₅:0.4MoO₃

PGPM₀:45PbO-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 subsequently annealed from 300°C with a cooling rate of 1°C/min. The ESR spectra of fine powders of the samples were recorded at room temperature using a JEOL JM-FX3 X-band ($\nu = 9.234$ GHz) ESR spectrometer with 100 kHz field modulation.

3.Results:

The ESR spectra, recorded at room temperature for PbO-Ga₂O₃-P₂O₅:MoO₃ glasses under investigation are shown in Fig. 1; spectra exhibit a central line surrounded by smaller satellites with $g_{\perp} = 1.945$ and $g_{\parallel} = 1.889$ due to paramagnetic Mo⁵⁺ ion. They may be attributed to the ⁹⁵Mo(15.7%) and ⁹⁷Mo(9.4%) isotopes which have the nuclear spin $I = 5/2$. The intense central line belongs to the ⁹⁶Mo isotope which has the nuclear spin $I = 0$. The intensity and the half width $\Delta B_{1/2}$ of the central line is found to increase with increase in the concentration of MoO₃. This parameter increases with increase in the concentration of MoO₃. Further the resolution of the hyperfine splitting goes on decreasing with increase in the concentration of MoO₃.

First derivative of absorption (arb. units)

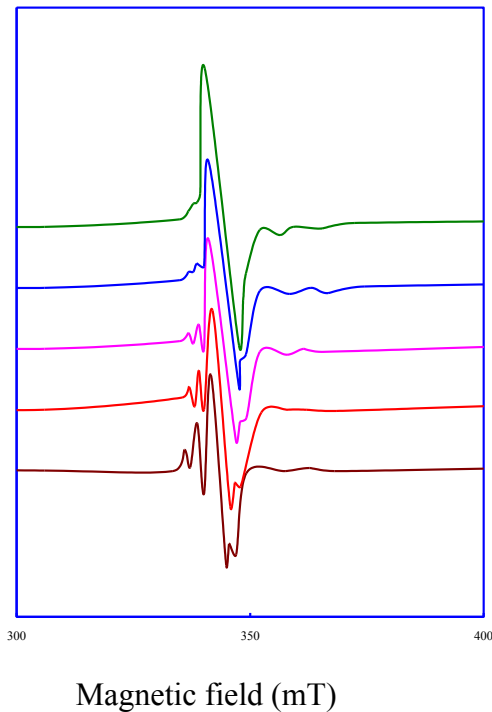


Fig1 ESR spectra of PbO–Ga₂O₃–P₂O₅: MoO₃ glasses recorded at room temperature. Inset shows the variation of intensity of the signal with concentration of MoO₃

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 [8]. 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) [9,10]. However, Bo may also participate in the glass network with PbO₄ structural units when lead ion is linked to four oxygens in a covalency 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.

The highest intensity of the signal observed in the ESR spectrum of the glass PGPM₅ 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 Mo^{5+} ions can be accounted for such variations. The variation of MoO_3 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 MoO_3 .

5. Conclusions:

ESR spectral studies indicated a gradual transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO_3 .

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