Electron Spin Resonance Studies of Mn(+2), Gd(+3) and Cu(+2) in Chalcogenide Glasses (Al$_2$S$_3$-La$_2$S$_3$ System)

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Abstract: The chalcogenide glass (ALS, Al$_2$S$_3$-La$_2$S$_3$) was prepared by melting a stoichiometric mixture of aluminum powder and La$_2$S$_3$ under H$_2$S atmosphere at 1200°C. Glasses containing 0.1 – 1.0 mol % of Mn^{2+}, Gd^{3+} and Cu^{2+} were also prepared. The characteristic features of the ESR spectra for the transition metal containing ALS glasses are interpreted.

INTRODUCTION

After the discovery of the unusual electrical and optical properties in chalcogenide glasses, such as switching,[1] memory[2] and imaging,[3] much of the attention has been directed towards obtaining information on the structure of these glasses and recent ESR studies [4-6] has been undertaken for the purpose of understanding the above mentioned phenomena.

The first ESR study of transition metal ions in glasses was made by Sands[7] who studied some 34 soda-lime-silica base glasses. Almost all of his samples had resonances at g=6 and at g=4.3 which he was then unable to explain. Subsequently, Castner et al[8] assumed crystal field effects to be dominant in their study of iron in a soda-lime-silica glass, and used the orthorhombic spin Hamiltonian to obtain an isotropic g value of 4.29. Wickman et al[9] extended the idea of Castner et al[8] and used the strong crystal field Hamiltonian to calculate all the possible g values for S=5/2. More recently, investigations have been made on Gd(+3) ions in soda-silica-yttria glasses,[10] and in YAG glass.[11]

Chalcogenide glasses in which the rare earth was a main constituent were first reported by J. Flahaut and his group.[12] The increasing interest devoted to amorphous solids containing rare earth ions has been stimulated by the quest of new material for lasers.

The present paper reports on the various properties of the ESR signals observed for

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some paramagnetic ions {Gd(+3). Cu(+2),   Mn(+2)} in ALS (Al_2S_3-La_2S_3) glasses. From these results we provided informations about the origin of these signals and some structural properties.

EXPERIMENTAL

(1) Preparation of Compounds

The following reactants were prepared according to published methods(13,14) and were identified by XRD. They are La_2S_3, MnS, Gd_2S_3, and CuS.

Chalcogenide glasses, $3Al_2S_3$-La_2S_3(ALS) was prepared by melting a stoichiometric mixture of aluminum powder and La_2S_3 at around 1200°C for 4 hours, then the melt was quenched in liquid nitrogen.   During the reaction, H_2S was passed through the reaction tube.

Glasses containing the compositions of ca. 0.1-1.0 mol% Mn(+2), Gd(+3) and Cu(+2) were obtained by adding stoichiometric amounts of the sulfides to the glass-forming mixture and react mentioned above.

(2) Measurements

X-ray diffraction pattern were taken with a powder diffractometer using Cu-K radition(Model D/MAX-3A, X-ray Diffractometer Rigaku Co.).

EPR spectra were recored on a Bruker EPR Spectrometer   (Model ER 200) equipped with a variable temperature accessories operating at X-band wavelength.

RESULTS and DISCUSSION

The X-ray analysis showed that the resultant samples were of a vitreous nature, i.e. no crystalline phase was found.

Mn(+2)   doped ALS glass

The characteristic features of these ESR spectrum shows two absorption lines centered at g=4.35 and g=2.00. The g=4.35 line is broad and asymmetric and its hyperfine structure is not well resolved. Theoretical analysis[15] predicts that an ion with S=5/2 in amorphous materials gives an ESR absorption at g=4.29, provided that the ion site has nearly rhombic symmetry and the fine structure constant is much larger than Zeeman energy. Hence, this signal is concluded to originated from Mn(+2) incorporated in   amorphous network.[16] The g=4.35 is indicative of a distorted crystalline field in the vicinity of manganese.

The hyperfine structure with A=68.3×10^{-4} cm^{-1} appears only for g=2.00. Probably this ESR line is due to Mn(+2) ions coordinated by four S atoms.[17] So obtained ESR data for Mn(+2) impurity ions and intrinsic paramagnetic centers indicate that these two types of paramagnetic probes are sensitive to the different structural peculiarities of the Al-La-S

glass network.

Gd(+3) doped ALS glass

The X-band EPR spectrum of a glass of nominal composition $3Al_2S_3$-La_2S_3 doped with Gd(+3) is recorded. This spectrum is a typical of the so-called U spectrum [18,19] which is the most frequent signature of S-state rare earth ions in glasses.

This spectrum consists of four essential features of effective g-values=2.0, 2.8, 3.5 and 5.9 etc. The form of the U spectrum is actually a consequence of the randomness characteristic of glasses and should not be approached from the view point of a few, specific well-defined site symmetries, even when the matrix is a crystalline phase.

In several previous studies,[8] involving complex resonances of smaller paramagnetic ions {Fe(+3), Mn(+2)}, the ion was postulated to exist in both a network forming and a network modifying site. In the present study, the possibility of Gd(+3) ion existing in a network forming site is eliminated. Due to the large ionic size of the Gd(+3) ion {r= 1.11Å, La(+3), 1.15Å }, it is unreasonable to assume that it can substitute for the smaller Al(+3) ion (r=0.5Å). If the Gd(+3) ion is restricted to the role of a network modifier in a homogeneous random network and exists no tendency toward some preferred symmetry, then the resonance spectrum would be characterized by a broad smear.

The complex spectrum found in vitreous ALS is apparently associated with Gd(+3) ions occupying various positions in the glass lattice, these being characterized by crystalline fields of different magnitude and symmetry. Thus the line with g=2.0 is probably due to Gd(+3) ions at sites giving a weak crystalline field of high symmetry. The narrow line with a g factor of g=5.9 and the peaks in the region of g=2.8 and 3.5 are possibly due to Gd(+3) ions lying in the glass lattice at positions associated with a strong crystalline field of low symmetry. The possibility of a strong crystalline field arising around the Gd(+3) ions in the vitreous Al-La-S system may be associated with the presence of certain ionic complexes distributed over the covalently connected glass lattice.

It is interesting to note that similar spectra have been observed in a variety of glasses doped with Gd(+3), for example methanol glass,[4] borate glasses [21,22], phosphate glasses[22], silicate glasses [22,23], comparing with that obtained here. Thus, it would appear that perhaps the Gd(+3) ion seeks out sites that furnish the same crystal field regardless of the origin of in terms of chemical constituents. The essential motion that will be repeatedly emphasized is that of the random character of the glass structure which has the consequence of engendering a continuous range of small distortion of the local symmetry at the ion sites. Therefore, there will be a random distribution in the crystal field (and spin Hamiltonian) parameters associated with each basic ion site.

A convincing argument can be made for the existence of more than one available site for the Gd(+3) ion. The laser spectra of several rare earth ions in glasses have led Etzel et al[24] and Snitzer[25] to suggest the existence of multiple sites.

The undoped and Cu(+2) doped ALS glass

The EPR spectrum of Cu(+2) in most oxide glasses is distinctive and easily recognized on the basis of the principal g values and a four line hyperfine splitting due to Cu and Cu(I=3/2 for both isotopes).

However Cu(+2) doped ALS glass shows a wide(ΔH=1100G) intense line with no rsesolved hyperfine structure, leading to the suspicion of a broad distribution of spin Hamiltonian and a sharp line with a g factor of about 2.0. The undoped ALS glass shows only a sharp line with a g factor of about 2.0 also.

Generally the various paramagnetic defect states could be induced by energetic radiations and many authors [26,27] have reported the study of radiation damage in some oxide glasses.

In our system, the sharp line of Cu(+2) doped and undoped ALS glasses are assumed to be induced by quenching from a melt, giving rise to a radical[28] in ALS glass.

The understandings of structural aspects and the electrical properties of this defect chalcogenide glass remain as a interesting problems.

Acknowledgement

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