

EPR studies of Gd^{3+} ions in lithium tetra boro-tellurite and lithium lead tetra boro-tellurite glasses

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Abstract

Glass systems of composition $85 Li_2B_4O_7 + (15-x) TeO_2 + x Gd_2O_3$ ($x = 0, 1, 2, 3, 4$ and 5 mol%) and $80 Li_2B_4O_7 + 10 PbO + 8 TeO_2 + 2 Gd_2O_3$ have been studied by using electron paramagnetic resonance (EPR). The EPR spectra indicate Gd^{3+} ions located at three types of sites randomly distributed in the host glass. The spectra exhibits three broad EPR signals at $g \approx 2.0$, $g \approx 2.8$ and $g \approx 5.4$ are attributed to Gd^{3+} ions located at sites with weak, intermediate and strong cubic symmetry fields respectively. In principle these sites may be of network forming and network modifying type. Ionic radius considerations suggest that gadolinium ions cannot substitute the much smaller boron ions and thus only the network modifier site is acceptable. The effect of gadolinium content as well as temperature $123-433$ K on resonance signals have been investigated. The number of spins (N) participating in resonance and its paramagnetic susceptibility (χ) for $g \approx 5.4$ resonance line have been calculated as a function of Gd content and temperature. It is observed that N and χ increase with x . A linear relationship was established between $\log N$ and $1/T$ and the activation energy was calculated from the graph. From the graph the Curie constant (C) and Curie temperature (θ) have been evaluated. The temperature dependence of inverse magnetic susceptibility ($1/\chi$) displays Curie-Weiss type of magnetic behaviour. The theoretical values of optical basicity (A_{th}) of the glasses have also been evaluated.

Keywords: Electron paramagnetic resonance; Gd^{3+} ions; Glasses

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1. Introduction

Research on tellurite and heavy metal oxide based glasses have stirred up significant interest in

the field of new glassy materials. These materials have shown high non-linear refractive index, high transmission in visible and near infrared region and optical non-linearity effect; hence they have become promising materials for applications in the non-linear optical devices such as optical switching, optical memory etc. [1–3]. It is known that TeO_2 in combination with modifiers, like PbO , forms stable glasses. The distinguished factor of these tellurite-based glasses is their weaker Te-O bonds; the atomic network appears more open than that in silica glasses. This exclusive structure character of tellurite glasses provides the possibility for them to be a good host of some rare earth and heavy metals with small multi phonon decay rates [4,5]. The Te-O bond in tellurite glasses is easily broken and this is an advantage for accommodating rare-earth (RE) ions and heavy metal oxides.

In the present investigations, we have prepared Gd^{3+} ions doped lithium tetra boro-tellurite and lithium lead tetra boro-tellurite glass systems. $\text{Li}_2\text{B}_4\text{O}_7$ has itself attracted much attention as a substrate for surface wave acoustic (SWA) devices. The material has cuts with temperature stability of acoustic wave velocity and high electromechanical coupling coefficient for SWA. Also, $\text{Li}_2\text{B}_4\text{O}_7$ with some dopants find applications in thermo-luminescent personal dosimeters [2,3]. The dopants like RE in glasses also acts as promising candidates for laser and other potential opto-electronic applications [6].

The study of RE ions in glasses by EPR technique gives information on the structure of the glass. Many studies were devoted to the analysis of the RE coordination structure, both through molecular dynamics simulation (and crystal field theory) [7–9] and by optical measurements [10–12]. A limited number of studies were also performed by analyzing the electron paramagnetic resonance (EPR) data [13–18]. No EPR studies of Gd^{3+} ions in lithium tetra boro-tellurite and lithium lead tetra boro-tellurite glasses have been reported so far. Hence the authors thoroughly studied the EPR spectra of Gd^{3+} ions in these glasses. We are also interested in studying the effect of Gd content and temperature (123–433 K) on resonance. The results obtained from these studies are discussed with respect to the composition as well as temperature.

2. Experimental

The glass samples were prepared by melt quenching technique. The starting materials $\text{Li}_2\text{B}_4\text{O}_7$, TeO_2 , PbO and Gd_2O_3 used in the preparation of the glasses were of Analar grade quality. The composition in mol% of glasses studied in the present work are $85 \text{Li}_2\text{B}_4\text{O}_7 + (15-x) \text{TeO}_2 + x \text{Gd}_2\text{O}_3$ ($x = 0, 1, 2, 3, 4$ and 5) (hereafter referred to as $\text{LTBTe}:x$) and $80 \text{Li}_2\text{B}_4\text{O}_7 + 10 \text{PbO} + 8 \text{TeO}_2 + 2 \text{Gd}_2\text{O}_3$ (hereafter referred to as $\text{LPTBTe}:2\text{Gd}$). The chemicals were weighed accurately in an electronic balance mixed thoroughly and ground to fine powder. The batches were then placed in porcelain crucibles and melted in an electrical furnace in air at their glass forming temperatures (i.e., 1230 K for half-an-hour). The melt was then quenched to room temperature in air by pouring it onto a polished porcelain plate and pressing it with another polished porcelain plate. The glasses thus obtained were transparent and colour less. The glasses were then annealed at 423 K for 3 h to remove the thermal strains. The glass formation was confirmed by powder X-ray diffraction recorded with a Phillips type PW 1050 diffractometer.

The EPR spectra were recorded on a EPR spectrometer (JEOL-FE-1X) operating in the X-band frequency (≈ 9.205 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT with a scan speed of 62.5mT min^{-1} and the microwave power used was 5 mW. A powdered glass sample of 100 mg was taken in a quartz tube for EPR measurements. Polycrystalline DPPH with a g value of 2.0036 was used as a standard field marker.

The EPR spectrum of $\text{LTBTe}:2\text{Gd}$ glass sample was recorded at different temperatures (123–433 K) using a variable temperature controller (JES UCT 2AX). A temperature stability of ± 1 K was obtained by waiting for half-an-hour at the set temperature before recording the spectrum.

3. Results and discussion

3.1. EPR studies

The EPR spectra of undoped samples show no signals confirming that the starting materials used

for the base glass are free from any paramagnetic impurities. The Gd^{3+} ions doped LTBTe and LPTBTe glasses exhibits three prominent resonance signals at $g \approx 2.0$, $g \approx 2.8$ and $g \approx 5.4$ with weak features at $g \approx 4.3$ and $g \approx 3.3$, a characteristic of so called U-spectrum of Gd^{3+} ions in disordered matrices (glasses) [19], which is the most frequent signature of S-state rare earth ions in glasses. EPR spectra of RE ions in glassy solids are generally very anisotropic and sensitive to variations in ligand field from site to site. Owing to this the EPR spectra of Gd^{3+} ions in glassy solids are far less intensively studied when compared to transition metal ions. The Gd^{3+} ions, when present in low concentrations in glassy host, usually exhibit three prominent signals with effective g -values of $g \approx 5.4$, 2.8 and 2.0 superimposed on a broad resonance line shape that encompasses the prominent $g = 2.0$ resonance signal. In addition to this weak signals at $g = 3.3$ and 4.3 are also observed. This type of spectrum has been aptly labeled as the U-spectrum [19] in view of its omnipresence in vitreous materials [20–32] as well as in disordered poly crystalline materials [19]. A typical EPR spectrum of 2 mol% doped Gd^{3+} ions in glass samples with and without lead content at room temperature is shown in Fig. 1. The spectrum is similar to U-spectra familiar in many oxides, fluoride and fluorozirconate glasses indicating very low and distorted site symmetries with a broad distribution of crystal fields. The EPR spectra with different x also exhibits similar type of resonance signals at $g \approx 2.0$, $g \approx 2.8$ and $g \approx 5.4$, in addition to the change in intensity. It is observed that intensity of the signals increases with x . Fig. 2(a) and (b) shows the EPR spectra of LTBTe:2Gd glass sample as function of temperature. From the figure it can be seen that the intensity of all the resonance signals were increased with decreasing temperature. Further, it can be seen that the g -value and line widths of all signals are independent of temperature.

An exact analysis of the U-spectrum is complicated by two factors. First, the randomness inherent in disordered systems, results in a broad distribution of crystal field parameters in comparison with that present in polycrystalline powders.

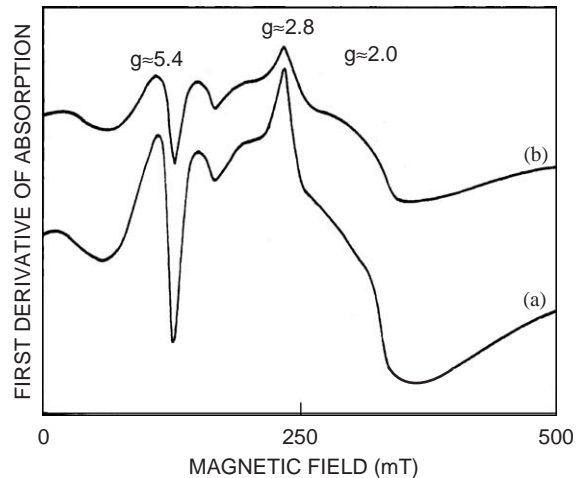


Fig. 1. EPR spectra of 2 mol% Gd^{3+} ions doped (a) lithium tetra boro-tellurite (LTBTe:2Gd) and (b) lithium lead tetra boro-tellurite (LPTBTe:2 Gd) glass samples at room temperature.

So, in the analysis of the U-spectrum, the average over the distribution of crystal field parameters must be considered, in addition to the usual powder angular average. Secondly, the EPR absorption curve of the U-spectrum has its maximum near $g \approx 2.0$, a second absorption near $g \approx 6.0$ and a significant amplitude at $g \approx \infty$ (zero field). This indicates that there is a wide range of crystal field strengths where neither the Zeeman interaction nor the crystal field interaction may be realistically treated by perturbation methods.

Different explanations were given by different authors [20,21,23,28] to explain the U-spectrum of Gd^{3+} ions in glasses. Chepeleva et al. [20] were the first to discuss the U-spectrum and they attributed the $g \approx 6.0$ resonance to a strong cubic field on the basis of solutions obtained for a ‘cubic’ Hamiltonian in the strong crystal field limit where the Zeeman interaction may be treated as a perturbation. Another, early but more detailed analysis of the U-spectrum was performed by Niklin et al. [21]. They searched extensively for a single set of ‘rhombohedral’ crystal field parameters that could simultaneously account for all the principal features of the U-spectrum, but they attributed the three prominent features to three distinct types of crystal fields. The $g \approx 6$ feature was attributed

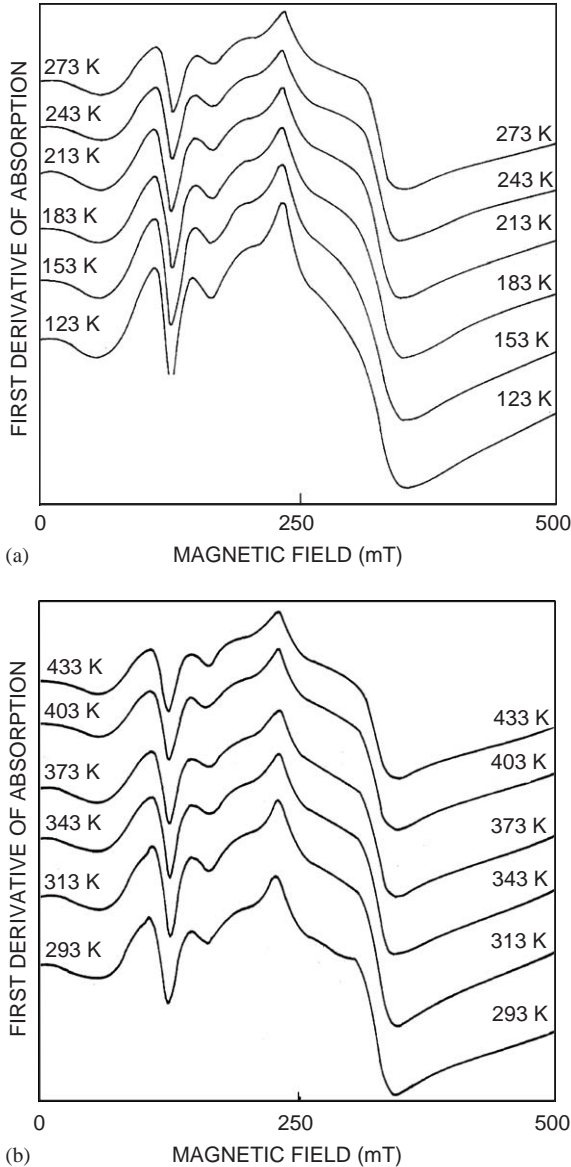


Fig. 2. (a) and (b) EPR spectrum of LTBTc:2Gd glass sample at different temperatures.

to a strong cubic crystal field, as in the interpretation given by Chepeleva et al. [20]. Cugunov and Kliava [23] and Koopmans et al. [28] employed computer simulation techniques in their analysis but their final interpretations differ from each other. Cugunov and Kliava [23] attributed the $g \approx 6.0$ to well defined rhombic crystal field and the

broad resonance encompassing $g \approx 2.0$ due to formation of Gd^{3+} clusters. In contrast, the $g \approx 6.0$ resonance was considered to be a feature characteristic of intermediate crystal field sites of axial symmetry and have attributed the broadened general appearance of the U-spectrum to isolated rare earth ions in a wide varieties of sites.

By taking into consideration a wide range of EPR data, Brodbeck and Iton [24] concluded that the glassy matrices containing the RE ions impose virtually no specific or narrowly defined, site symmetries on the RE ions with the result that the RE ions can coordinate with a relatively large number of irregular ligands. In addition to that they found the U-spectrum is expected to prevail only when the RE S—state ions are able to achieve a high coordination number (≥ 6) within the structurally disordered matrices. Thus, the site symmetries of the RE ions in glasses are essentially low and disordered which dictate their own environments in glasses and are best characterized by a single low symmetry type-sites as proposed by Griscom [22]. Therefore, in conclusion, it can be pointed that the Gd^{3+} ions are generally suspected to improve their environment when present in glass systems as impurities. The very similar spectral features of Gd^{3+} ions in different glassy hosts [20–32] supports this argument. Another recent work by Legein et al. [29] followed a similar approach and attributed the U-spectrum to isolated Gd^{3+} ions in a variety of sites with a coordination number generally estimated to be 8 or 9 in tetrahedral network glasses with a distribution of spin-Hamiltonian parameters. Nevertheless, a full agreement with this view is not yet established. Other workers based their analysis on the assumption that each contribution at $g \approx 5.4, 2.8$ and 2.0 to the U-spectrum would arise from distinct coordination symmetries of the Gd^{3+} ion [14–16], despite the fact that Brodbeck and Iton had made evident the inconsistency of this interpretation, already present in previous studies [23,28].

In conclusion, it can be pointed that the Gd^{3+} ions are generally suspected to impose their own environment when present in glass systems as impurities. In the present work, the EPR spectrum consists of three essential features with effective

g -values $g \approx 5.4$, 2.8 and 2.0 and weak features at $g \approx 3.3$ and 4.3. The three EPR signals at ($g \approx 2.0$, $g \approx 2.8$ and $g \approx 5.4$) are due to Gd^{3+} ions located at sites with weak, intermediate and strong cubic symmetry fields respectively. In principle these sites may be of network forming and network modifying type. Ionic radius considerations suggest that gadolinium ions cannot substitute the much smaller boron ions and thus only the network modifier site is acceptable. The resonance at $g \approx 2.0$ is due to the Gd^{3+} ions situated in a cubic symmetry for which the crystal field parameters are distributed in an extended range of values. It is also observed that the intensity of the resonance signals is low in lithium lead tetra borate glasses compared to lithium tetra borate glasses.

In boro-tellurite glasses both B_2O_3 and TeO_2 are present, it leads to complex specification in the glass structure [33]. The species present in the glasses can be $[BO_{4/2}]^- (\equiv B_4^-)$ and $[BO_{3/2}]^- (\equiv B_2^-)$, trigonal bipyramidal (tbp) $[TeO_{4/2}]^0 (\equiv T_4^0)$ and trigonal pyramidal (tp) $[TeOO_{2/2}]^0 (\equiv T_2^0)$ along with tbp $[TeO_{3/2}O]^- (\equiv T_3^-)$ and tp $[TeO_{1/2}O]^- (\equiv T_1^-)$ [34–38] (note: the superscript on letters B and T represents the charge and the subscript represents the number of bridging oxygens attached to the central atom). Besides, in this glass system there are three structural conversion reactions of interest, viz. $B_4^- \rightarrow B_2^-$, $T_4^0 \rightarrow T_2^0$ and $T_4^- \rightarrow T_1^-$. These conversions are promoted when the concentration of the modifier, is increased. $T_4^0 \rightarrow T_2^0$ conversion also appears to be promoted by the presence of ionic salts/alkali oxides. The introduction of alkali oxides to TeO_2 changes the Te coordination polyhedron from TeO_4 to TeO_3 trigonal through breaking Te–O–Te bonds [39,40].

Addition of PbO to TeO_2 also causes some coordination changes in Te, but the tendency of Te to decrease the coordination number with increasing PbO was smaller than in alkali-tellurite glasses [41]. The weaker tendency of PbO for changing the coordination state of Te is explained in terms of the higher covalency of Pb–O bonds. This means that the major part of PbO behaves as a glass former in the high lead containing glasses [42]. However, in the present study, we have introduced little amount of PbO , the lead oxide enters the

glass as an intermediate between a network former and a network modifier and increases the number of nonbridging oxygens in the glass network. The very strong covalent nature of the lead with the oxygen distorts the TeO_4 tetrahedra and facilitating more number of nonbridging oxygens. In oxide glasses, RE ions coordinate with nonbridging oxygen. Therefore Gd^{3+} will coordinate more with excess non-bridging oxygens, available in lead contained glass and there by reduce the number of individual Gd^{3+} ions. This may be the reason for the reduced in resonance intensity in lead doped glass.

3.2. Calculation of number of spins participating in resonance

The number of spins participating in a resonance can be calculated by comparing the area under the absorption curve with that of a standard ($CuSO_4 \cdot 5H_2O$ in this study) of known concentration. Weil et al. [43] gave the following expression which includes the experimental parameters of both sample and standard:

$$N = \frac{A_x(\text{Scan}_x)^2 G_{\text{std}}(B_m)_{\text{std}}(g_{\text{std}})^2 [S(S+1)]_{\text{std}}(P_{\text{std}})^{1/2}}{A_{\text{std}}(\text{Scan}_{\text{std}})^2 G_x(B_m)_x(g_x)^2 [S(S+1)]_x(P_x)^{1/2}} [\text{Std}], \quad (1)$$

where A is the area under the absorption curve which can be obtained by double integrating the first derivative EPR absorption curve, scan is the magnetic field corresponding to unit length of the chart, G is the gain, B_m is the modulation field width, g is the g factor, S is the spin of the system in its ground state. P is the power of the microwave. The subscripts ‘x’ and ‘std’ represent the corresponding quantities for Gd^{3+} glass sample and the reference ($CuSO_4 \cdot 5H_2O$) respectively. The [Std] used in Eq. (1) is the area under the absorption curve ($CuSO_4 \cdot 5H_2O$ in this study), which is obtained by numerical double integrating the first derivative EPR spectrum of known concentration. The number of spins participating in resonance (N) for $g \approx 5.4$ resonance line have been calculated in lithium tetra boro-tellurite glasses with and without lead content. It is observed that the number of gadolinium spins

participating in resonance is more for lithium boro-tellurite glasses without lead content compared to those having lead content. This can be seen clearly from the peak-to-peak heights of the EPR spectra of LTBTe and LPTBTe glass samples at room temperature (Fig. 1). From the Fig. 1 it can be seen that the peak-to-peak height for LTBTe:2Gd is more compared to that of LPTBTe:2Gd glass sample. The decrease in spins with lead content is due to the same reason as discussed earlier.

The temperature dependence of number of spins participating in resonance for $g \approx 5.4$ resonance line in LTBTe:2Gd glass has been calculated using the above Eq. (1). A graph between logarithm of number of spins against reciprocal of absolute temperature shown in Fig. 3. From the graph it is found that the number of spins decreases with increase of temperature. Further, a linear relationship is observed between $\log N$ and $1/T$ in accordance with the Boltzmann law. The activation energy can be calculated from the slope of the graph. The activation energy, thus calculated is found to be 1.951×10^{-21} J (0.012 eV).

3.3. Calculation of paramagnetic susceptibility (χ) from EPR data

The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the

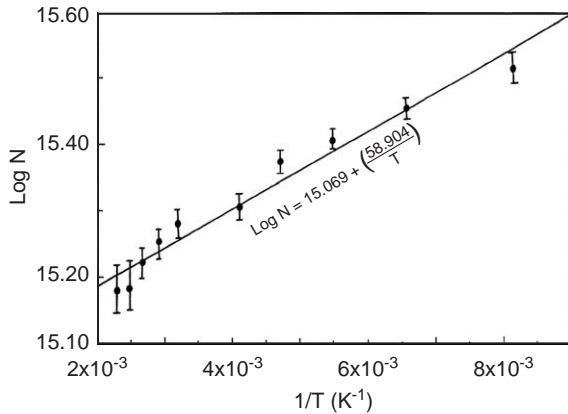


Fig. 3. A variation of $\log N$ versus $1/T$ for LTBTe:2Gd glass sample.

formula [44]

$$\chi = \frac{Ng^2\beta^2J(J+1)}{3k_B T}, \quad (2)$$

where N is the number of spins per kg, which can be calculated from Eq. (1) and the other symbols have their usual meaning. g are taken from EPR spectrum. Fig. 4 shows a plot between $1/\chi$ and absolute temperature (T). The graph is a straight line with a positive slope and it is interesting to observe that it obeys Curie–Weiss law. From the graph the Curie constant (11.82×10^{-3} emu mol $^{-1}$) and Curie temperature (92.7 K) have been evaluated.

3.4. Optical basicity of the glass (A_{th})

Duffy and Ingram [45] reported that the ideal values of optical basicity can be predicted from the composition of the glass and the basicity moderating parameters of the various cations present. The optical basicity of an oxide glass will reflect the ability of the glass to donate negative charge to the probe ion [46]. The theoretical values of optical basicity of the glass can be estimated using the formula [45]

$$A_{th} = \sum_{i=1}^n \frac{Z_i r_i}{2\gamma_i}, \quad (3)$$

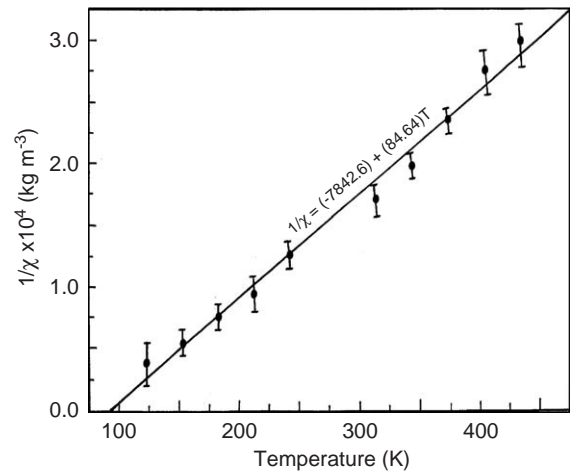


Fig. 4. A plot of reciprocal susceptibility ($1/\chi$) versus T for LTBTe:2Gd glass sample.

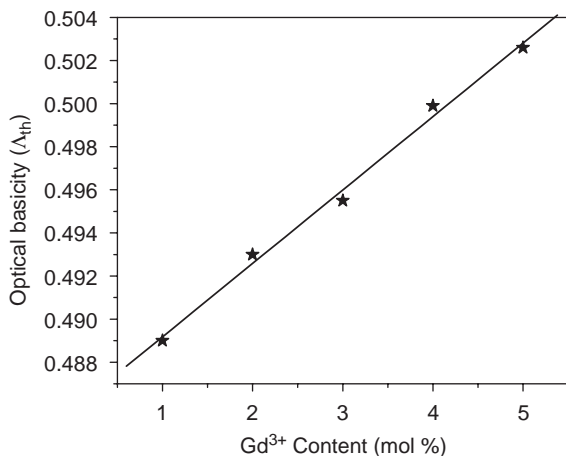


Fig. 5. The variation of theoretical values of optical basicity (A_{th}) of the LTbTe:xGd glass samples as a function of Gd^{3+} content.

where n is the total number of cations present, Z_i is the oxidation number of the i th cation, r_i is the ratio of number of i th cations to the number of oxides present and γ_i is the basicity moderating parameter of the i th cation. The basicity moderating parameter γ_i can be calculated [45] from the following equation:

$$\gamma_i = 1.36(x_i - 0.26), \quad (4)$$

where x_i is the Pauling electronegativity [47] of the cation. The theoretical values of optical basicity (A_{th}) are calculated for all the glass samples as a function of Gd^{3+} content as shown in Fig. 5. It is interesting to observe that the optical basicity increases linearly with x .

4. Conclusions

The EPR spectra of Gd^{3+} ions in lithium tetra boro-tellurite and lithium lead tetra boro-tellurite glasses exhibits three broad EPR signals at $g \approx 2.0$, $g \approx 2.8$ and $g \approx 5.4$ are attributed to Gd^{3+} ions located at sites with weak, intermediate and strong cubic symmetry fields respectively. In principle these sites may be of network forming and network modifying type. Ionic radius considerations suggest that gadolinium ions cannot

substitute the much smaller boron ions and thus only the network modifier site is acceptable. The EPR spectra indicate Gd^{3+} ions located at three types of sites randomly distributed in the host glass. The number of spins (N) participating in resonance and its paramagnetic susceptibility (χ) for $g \approx 5.4$ resonance line have been calculated as a function of Gd content and temperature. It is observed that N and χ increase with x . A linear relation was established between $\log N$ and $1/T$ and the activation energy was calculated from the graph. The reciprocal of susceptibilities ($1/\chi$) are found to vary a Curie–Weiss type of magnetic behaviour. From the plot the Curie constant and Curie temperature have been evaluated.

Acknowledgements

Dr. RPSC is grateful to the Science and Engineering Research Council SERC, (Department of Science and Technology, DST) New Delhi, for the award of Fast Track research project under Young Scientist scheme.

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