

# Rare-earth ion-assisted nuclear spin-lattice relaxation in Nd<sup>3+</sup>-doped binary sodium borate glasses: <sup>11</sup>B NMR study

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Rare-Earth (RE) doped glasses are promising candidates for laser and other opto-electronic applications. The optical properties of the RE doped glasses depend on the symmetry and environment of the RE ion in the host glass and hence its structure. We have studied Nd<sup>3+</sup> doped 30Na<sub>2</sub>O-(70-x)B<sub>2</sub>O<sub>3</sub>-xNd<sub>2</sub>O<sub>3</sub> glasses with various Nd<sup>3+</sup> concentrations ( $x=0, 0.1, 0.5, 1$  mol%) using <sup>11</sup>B NMR. In this paper we have presented a method of estimating the crystal field splitting of the RE ion using <sup>11</sup>B Nuclear Spin-Lattice Relaxation (NSLR) time measurements in these systems as a function of temperature in the range 100–4.2 K. Details of the magnetization recovery fit, theory of <sup>11</sup>B relaxation time are discussed in terms of possible relaxation mechanisms in the presence of a RE ion. We found that the relaxation can be explained using a two-level system (TLS) model for  $x=0$  and the Orbach process for other samples. The magnetization recovery is observed to fit better to a single exponential model in all the samples as evident from the statistical analysis of the fit. The crystal field splitting ( $\Delta$ ) estimated from our studies are found to be around 100 cm<sup>-1</sup>, in agreement with other Nd<sup>3+</sup>-doped systems reported in the literature.

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## I. INTRODUCTION

Rare-earth-doped glasses, containing a small to moderate concentration of rare-earth oxides have become promising candidates for laser and other optoelectronic applications over the past few years. The effect of doping of rare-earth ions in various host glass systems like silicates, phosphates, borates, fluorides, etc. on different properties of the host glass have been studied and reviewed in the literature.<sup>1,2</sup> The RE ion can exist in different environments in the glass matrix depending on its structure, and a study of the environment around the RE ion is essential to understand the optical properties of such RE-doped glasses. Unlike crystals, the inherent disorder in glasses leads to the site to site variation of local bonding and symmetry. EXAFS,<sup>3,4</sup> optical methods like UV-VIS spectroscopy<sup>5,6</sup> and fluorescence studies<sup>1,7</sup> can give the average coordination number, bond lengths, local symmetry or covalency of bonds between the RE ion and the first shell neighbors. In a few cases nuclear spin-lattice relaxation dynamics has been used to understand the nature of clusters in certain RE-doped silicate glasses.<sup>8</sup> The other method, which is employed to get such information in crystals is the ESR technique, but is not suitable for RE-doped glasses to obtain meaningful results.<sup>9</sup> Recently Goudemond *et al.*<sup>10,11</sup> have shown that in rare-earth-doped metaphosphate glasses, containing different RE ions like Er, Nd, Sm, and Gd, the NSLR time measurements of <sup>31</sup>P could be used to monitor the RE ion dynamics in the temperature range from 100 K to 4.2 K.

Here we have explored the possibility of using a similar type of measurements in RE-doped binary alkali borate glasses as they are not only important for optical applications, but also form an interesting class of glasses to study the effect of the alkali ion on the glass forming network, particularly around the rare-earth ions. Borate glasses are structurally more intricate compared to silicate or phosphate

glasses, owing to the presence of different coordinations of boron. It is well established that the addition of an alkali oxide converts the boron coordination and the structural groups from one to another depending on the type and concentration of the alkali oxide.<sup>12</sup> In this paper we report <sup>11</sup>B NMR SLR time ( $T_1$ ) measurements in Nd<sup>3+</sup>-doped binary sodium borate glasses 30Na<sub>2</sub>O-(70-x)B<sub>2</sub>O<sub>3</sub>-xNd<sub>2</sub>O<sub>3</sub> ( $x=0.1, 0.5, \text{ and } 1$  in mol%) over a temperature range of 100–4.2 K. These  $T_1$  measurements are used to extract the magnitude of the crystal field splitting, to a fair accuracy, to understand the local structure around the RE ions.

In general, the magnetization recovery of a quadrupole nucleus in glass, in the presence or absence of paramagnetic impurities, is expected to be nonexponential. To examine the nonexponential nature of magnetization recovery in the absence of paramagnetic impurities we have also studied 30Na<sub>2</sub>O-70B<sub>2</sub>O<sub>3</sub> glass (henceforth referred to as  $x=0$  or undoped glass). In this paper we describe a method of evaluating <sup>11</sup>B  $T_1$  in the RE-doped binary sodium borate glasses (which can be extended to other RE-doped binary borate glasses), and get information on how the environment around the RE ions changes with the host glass structure by evaluating the magnitude of the crystal field splitting.

## II. THEORY

The temperature dependence of NSLR time in different undoped glasses has been investigated for different nuclei by a few groups.<sup>13–15</sup> In these glasses the variation of  $T_1$  with temperature at low temperatures (much less than the corresponding Debye temperature of the sample) could be explained using the phenomenological two-level system (TLS) model proposed by Anderson *et al.*,<sup>16</sup> and independently by Phillips.<sup>17</sup> This temperature dependence of  $T_1$  is found to be independent of the glass composition and the nucleus stud-

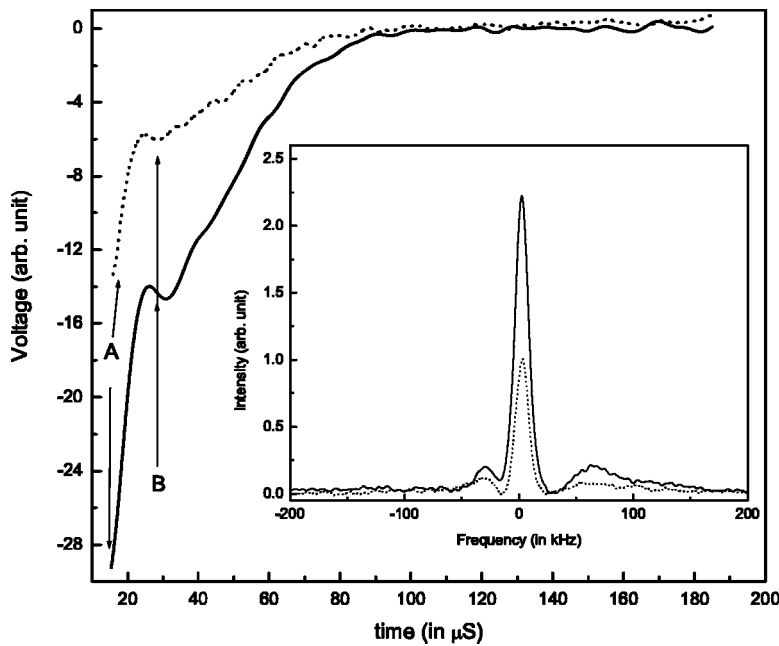


FIG. 1. FIDs and their FFTs of the  $^{11}\text{B}$  signal for the samples with  $x=0$  (dotted line) and  $x=1$  (full line).

ied, and varies as  $T^{-n}$ , where  $T$  is the temperature in K, and  $n$  is slightly more than 1 (Ref. 18).

When doped with a paramagnetic impurity, the relaxation is expected to be dominated by relaxation through the paramagnetic center. The temperature dependence of the nuclear relaxation time  $T_1$  follows the temperature dependence of the electron correlation (relaxation) time ( $\tau_e$ ), assuming that the paramagnetic ion concentration is low enough to neglect the interactions among themselves.<sup>19</sup> At sufficiently low temperatures the relaxation is dominated by the spin-diffusion to the paramagnetic centers, which in turn give the energy to the lattice. There are two limits which can be distinguished in the relaxation process. The first limit, dominant at low temperatures (when  $\tau_e \sim T_2$ ), is known as the diffusion limited region (DL), whereas the other limit, known as the rapid diffusion region (RD), is dominant at a relatively higher temperature (when  $\tau_e \ll T_2$ ). However, at still higher temperatures a usual dipolar (in the case of a spin- $\frac{1}{2}$ ) or quadrupolar (in the case of spin  $> \frac{1}{2}$ ) interaction provides the mechanism for spin-lattice relaxation. In the DL case, for a dipolar nucleus, the SLR time is given by<sup>10,20</sup>

$$\frac{1}{T_1} = \frac{4}{3} \pi n_s C^{1/4} D^{3/4}. \quad (1)$$

Here,  $C$  is given by

$$C = \frac{2}{5} (\gamma_I \gamma_S \hbar)^2 S(S+1) \frac{\tau_e}{1 + \omega_0^2 \tau_e^2}, \quad (2)$$

where  $D$  is the diffusion coefficient of the nuclear spin,  $n_s$  is the concentration of the impurity,  $\omega_0$  is the nuclear Larmor frequency, and  $\tau_e$  is the electron correlation time.  $\gamma_S$  and  $\gamma_I$  are the gyromagnetic ratios of electronic and nuclear spins, respectively, and  $S$  is the electron spin quantum number.

### III. EXPERIMENTAL

$30\text{Na}_2\text{O}-(70-x)\text{B}_2\text{O}_3-x\text{Nd}_2\text{O}_3$  (mole %) samples were prepared for four concentrations of  $\text{Nd}_2\text{O}_3$  ( $x=0, 0.1, 0.5$ , and 1) by taking appropriate weights of AR grade (purity  $>99.5$ )  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{Nd}_2\text{O}_3$  as starting materials and by the usual melt quenching technique. Samples with  $x=0$  were transparent and colorless, while the other samples were also transparent, but with a bluish tinge. The amorphous nature was confirmed by x-ray powder diffraction.

The  $^{11}\text{B}$  NSLR time was measured at 26.04 MHz (1.923 Tesla), using a home built pulsed NMR spectrometer around a 8 Tesla variable field superconducting magnet from *OXFORD Instruments*. Approximately 150 mg of powdered sample sealed in a quartz tube was used for the measurements. The spectrometer is capable of delivering a rf power of 1 kW to a load of  $50\Omega$ , with a dead time of 8–12  $\mu\text{s}$  depending on the temperature of the sample coil. Typical Free Induction Decay (FID) signals following a single  $\pi/2$  pulse and their absorption spectra (obtained from the FFT of the FIDs) for  $x=0$  (at 98 K) and  $x=1$  (at 110 K) are shown in Fig. 1. The FIDs show a structure consisting of a fast and a slow component of magnetization recovery. The FFT of the FID also consist of a broad signal from  $\text{BO}_3$  units and a narrow signal from  $\text{BO}_4$  units in agreement with the earlier report,<sup>12</sup> and is qualitatively similar for the doped and undoped glasses indicating that the boron environments in these glasses do not change in the presence of paramagnetic impurities. The spin echo signal also shows similar features as seen in the FID. A typical  $\pi/2$  pulse width used was 3–4  $\mu\text{s}$ . However, a  $\pi$  pulse could not be defined for any of the samples probably due to the broad lineshape originating from  $\text{BO}_3$  units. To measure  $T_1$  we have used a saturation burst sequence consisting of 150–200 preparation pulses ( $\pi/2$  pulses) with 300–500  $\mu\text{s}$  delay between them and then monitored with another  $\pi/2$  pulse at different delay times. The  $\pi/2$  pulse widths at different temperatures have been

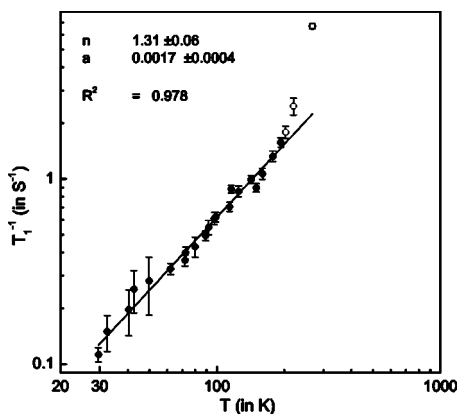


FIG. 2. The variation of  $T_1^{-1}$  with  $T$  for the  $x=0$  sample. The solid line is the fit to the equation  $T_1^{-1}=aT^n$ . The open points are not considered for fitting.

decided by seeing the amplitude of FID or spin-echo maximum, and is comparable to the  $\pi/2$  pulse width for the  $^{11}\text{B}$  nucleus in crystalline  $\text{NaBF}_4$ , for which a  $\pi$  pulse can be defined. As the quadrupolar coupling constant for  $\text{BO}_3$  and  $\text{BO}_4$  units are estimated to be around 2.6 MHz and 0.6 MHz, respectively,<sup>12</sup> in binary alkali borate glasses, we do not expect to excite any satellite transitions in our experiment.  $T_1$ 's were determined by taking the amplitude of the FID's at point A (indicated in Fig. 1) for the maximum S/N ratio. Measurements taken at the point B, gave similar values for  $T_1$ , but with a larger error due to a poor S/N ratio. To rule out the contributions to the FID from the receiver artifacts,  $T_1$ 's were also measured using the spin echo amplitudes at two different time windows using a progressive saturation method.<sup>21</sup> This method also gave similar values for  $T_1$  as obtained from the amplitude measurement of FID's.

#### IV. RESULTS AND DISCUSSION

The magnetization data was fitted to a single exponential recovery function. Although in some cases, particularly at low temperatures, we have seen a nonexponential nature in the initial part of the magnetization recovery, we have assumed an effective single exponential recovery model as reported in the literature<sup>22</sup> (as will be discussed in detail in Sec. IV A). Figure 2 shows the variation of  $T_1^{-1}$  with  $T$  obtained for the  $x=0$  sample in our study, and the fit to the equation  $T_1^{-1}=aT^n$  in the temperature range 200 K to 30 K. We get the value of  $n$  as 1.31(6), which is in good agreement with the reported results. Above 200 K  $T_1^{-1}$  deviates from this fit which can be attributed to the onset of the classical reorientational motions of different boron groups. In the doped glasses, the RE ions can have two possible coordinations depending on the glass composition as indicated by optical and EXAFS measurements. The optical studies<sup>5</sup> have indicated only 8 coordinated RE ions, while recent EXAFS studies<sup>3</sup> have indicated that they can occupy an octahedral symmetry site with 6 coordination when they coordinate to the nonbridging oxygen ion sites, apart from the usual 8 coordination with the negatively charged  $\text{BO}_4$  sites in a distorted cubic environment. In the case of  $\text{Nd}^{3+}$  ions, the crys-

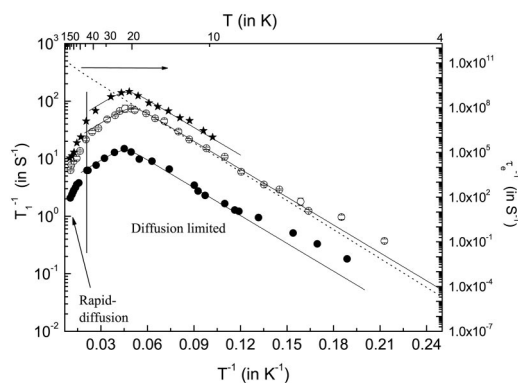


FIG. 3. The variation of  $T_1^{-1}$  with  $T$  for samples with  $x=0.1$  (●),  $x=0.5$  (○), and  $x=1$  (★). The solid line is the fit to Eq. (1), retaining only the Orbach process in Eq. (3). The error bars are shown only for the  $x=0.5$  sample; for all the  $T_1$  values the error is within 10%. The dotted line is the simulated curve for  $\tau_e$  for the  $x=0.5$  sample, using the parameters given in Table I.

tal field splits the  $^4\text{I}_{9/2}$  ground state into five Kramers doublets, whose degeneracy is lifted in the presence of the magnetic field and electronic transition between the two levels which are separated by an energy gap of  $\hbar\omega_e$  (where  $\omega_e$  is the electronic Larmor frequency) are possible. The RE ions in a solid can relax (electron spin-lattice relaxation) through different phonon mediated processes like direct (single phonon), Raman (two phonon), and Orbach process (two phonon) depending on the spin of the rare-earth ion and the temperature range.<sup>23,24</sup> Unlike the first two the Orbach process involves an electronic transition between two Zeeman split levels belonging to two lowest crystal field split levels, by an energy  $\Delta \gg \hbar\omega_e$ . For a Kramers ion,  $\tau_e$ , the electron relaxation rate in the presence of these three relaxation processes is given by<sup>23,24</sup>

$$\frac{1}{\tau_e} = \frac{1}{C_D \Delta^2} T + \frac{1}{C_R \Delta^2} T^7 + \frac{\Delta^3}{C_O} \frac{1}{\exp\left(\frac{\Delta}{k_B T}\right) - 1}, \quad (3)$$

where  $C_D$ ,  $C_R$ , and  $C_O$  are the relaxation constants for the direct, Raman, and Orbach process, respectively. Figure 3 shows the variation of the  $^{11}\text{B}$  relaxation rate,  $T_1^{-1}$  with temperature for the three doped samples and simulated electron relaxation rate for the  $x=0.5$  sample. The data have been fitted to the Eq. (1) in the temperature range between 45 K to 4.2 K which is the diffusion limited region for these samples assuming that only the Orbach process in Eq. (3) is responsible for the electron relaxation. The transition from the diffusion limited case to rapid diffusion case happens over a temperature range, revealed as a change of slope in  $T_1^{-1}$  versus  $T$  plot (Fig. 3). This has been represented by the dotted vertical line in the figure, and occurs in the same temperature range for all the three samples studied. Table I gives the values of the various fit parameters for these samples. Generally one expects a modification in the values of  $\Delta$  used in Eq. (3) incorporating a distribution of the crystal field splitting due to the randomness in the glassy matrix. But surprisingly our data fit well to the model with a single  $\Delta$

TABLE I. Values of the fitting parameters for  $x=0.1$ ,  $x=0.5$ , and  $x=1$  samples.

$x$ (in mol%)	$\Delta$ (in $\text{cm}^{-1}$ )	$C_O$ (in $10^{-5} \text{ sK}^3$ )	$n_s \times D^{3/4}$ (in $3.7 \times 10^9$ $(\text{m}^2\text{s})^{-3/4}$ )	$R^2$
0.1	103(5)	2.5(5)	4.7(1)	0.987
0.5	104(4)	1.2(2)	24.9(4)	0.994
1.0	102(5)	1.9(5)	48(1)	0.984

value. This is consistent with the earlier reports of similar measurements<sup>10,11</sup> in RE-doped metaphosphate glasses. The variation of the local structure around the RE ion from site to site is expected to give rise a distribution of the  $\Delta$  value. An estimate of this distribution is generally obtained from the UV-VIS spectroscopy from the line-width of the absorption spectra of different optical transitions.<sup>6</sup> In crystalline material doped with rare-earth ions, generally these spectral lines are well resolved upto the crystal field manifold levels. Recently Hehlen *et al.*<sup>25</sup> have shown from the  ${}^4I_{15/2} \leftrightarrow {}^4I_{13/2}$  optical transition in  $\text{Er}^{3+}$ -doped soda-lime and aluminosilicate glasses that the inhomogeneous broadening due to site to site variation of the crystal field of these transitions are significantly smaller than the overall crystal field splitting of those multiplets. This distribution in  $\Delta$ , inferred from the room temperature optical absorption spectra, may be grossly overestimated. Our results indicate that the immediate surroundings of the RE ions may not be very different from site to site in these glasses. The variation of  $n_s \times D^{3/4}$  with the mole fraction  $x$  of  $\text{Nd}_2\text{O}_3$  is linear indicating that there is no loss of rare-earth oxide during the preparation of the glasses and the  $T_1$  behaves in a predictable way with impurity concentration. Since this value has been evaluated as one of the fitting parameters from Eq. (1), the linear variation of it with  $x$  also cross checks the validity of the single exponential model used to evaluate  $T_1$ . We have estimated the value of diffusion coefficient  $D$  from the value of  $n_s \times D^{3/4}$  for the  $x=1$  sample obtained from the fitting shown in Fig. 3, using the density of a glass with almost a similar composition as ours, reported by Gatterer *et al.*<sup>6</sup> The value turns out to be  $\sim 10^{-17} \text{ cm}^2/\text{s}$ , which is three orders of magnitude less than the  $D$  values reported for a spin- $\frac{1}{2}$  nucleus in transition metal-doped crystals<sup>19</sup> and in RE-doped meta-phosphate glasses.<sup>11</sup> However, estimating the value of  $D$  from the nuclear line width, as reported in Ref. 11, will not be applicable for a spin- $\frac{3}{2}$  system, particularly in our case, where the nuclear line width is mainly due to the quadrupolar broadening. In such cases, the estimation of  $D$  as a fit parameter in the model for  $T_1^{-1}$  vs  $T$  variation appears to be a simple alternate way. A low value of  $D$  ( $\sim 10^{-17} \text{ cm}^2/\text{s}$ ) as obtained here may be due to the weak dipolar coupling of  ${}^{11}\text{B}$  nuclei, and/or due to the poor connectivity of the like spins (because of the low packing fraction) in glassy network compared to corresponding crystals.

In the doped glasses the radius of the sphere of influence increases as temperature decreases.<sup>9</sup> The NMR signal is observable until the spheres of influence overlap with each other. As expected, the signal vanishes at higher tempera-

tures for samples with more concentration of paramagnetic impurity. For example, in the case of the  $x=1$  sample the signal vanishes around 10 K as compared to the other two samples.

For  $x=0.1$  and  $x=0.5$ , we see a clear trend of deviation of the data at low temperatures from the assumed model. The values of  $T_1^{-1}$  appear to be higher than those predicted by the model. This could not be accounted by invoking a direct process or Raman process along with the Orbach process, or independent  ${}^{11}\text{B}$  nuclear relaxation through TLS. Incorporating a distribution of the  $\Delta$  values in Eq. (3) may not account for this deviation since the exponential nature of the fitting equation of the  $T_1$  values are not sensitive to the changes in the  $\Delta$  values at lower temperatures. Moreover, the regression coefficient for all the fits are reasonable enough to accept the present model. Further, at low temperatures the electronic relaxation can be modified by the interaction of electron with the TLS modes<sup>26-28</sup> which may account for this deviation. Since the magnitude of crystal field splitting is dependent on the environment around the RE ions, these measurements can be used to probe the structure of the host glass, especially around the RE ions.

#### A. Magnetization recovery

If only the central transition is excited of a spin- $\frac{3}{2}$  nucleus in crystals with a noncubic symmetry environment or with cubic symmetry distorted by the lattice imperfections, and in the absence of extreme motional narrowing, the nuclear magnetization recovery is expected to be bi-exponential.<sup>29,30</sup> However, in glasses, spectral and spatial inhomogeneity can give rise to further nonexponential behavior in nuclear magnetization recovery. In the case of a spectral inhomogeneity, the relaxation rate for a particular group of nuclei having the same Larmor frequency can be different from another group of nuclei, which have a slightly different Larmor frequency. On the other hand, the spatial inhomogeneity may lead to different microscopic clusters, with slightly different properties, like the correlation time and the activation energy of the relaxing modes. This in turn may give rise to a stretched exponential recovery of the magnetization in glasses as observed in proton glasses.<sup>31</sup> When doped with paramagnetic ions, the nuclei within the sphere of influence of the paramagnetic ion relax directly by the noise field generated by the paramagnetic ion following a magnetization recovery, given by  $\exp[-(t/T_1)^{1/2}]$  (Ref. 32). The nuclei, outside this sphere of influence, maintain a common spin temperature by a dissipative spin diffusion process and relax to the lattice via the paramagnetic center. The dissipative spin diffusion is an irreversible polarization transfer process induced by dipolar interactions and conserves the Zeeman energy of the involved spin pairs. The spatial spin diffusion for dipolar nuclei has been well studied.<sup>19</sup> The spatial spin diffusion *via* dipolar interaction between participating spin partners is a dominant one for a system of equivalent quadrupolar spins. The nuclei in the diffusive region relax with an exponential decay of magnetization. The magnetization recovery of spin- $\frac{3}{2}$  nuclei in glasses, particularly when paramagnetic impurity is present, can be fitted to a few models, involving in general

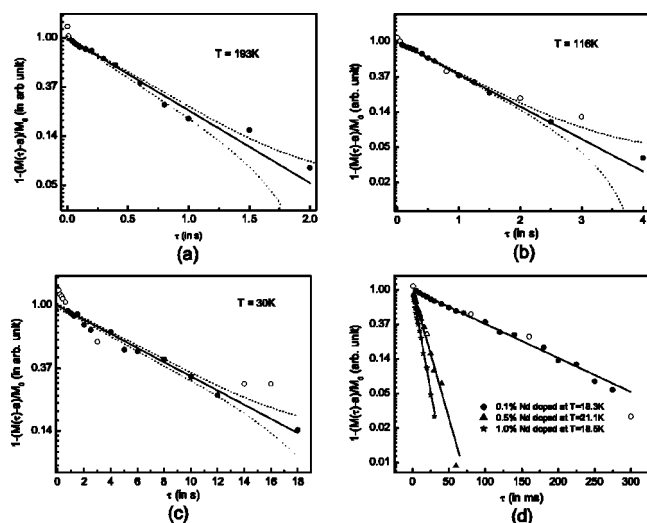


FIG. 4. Magnetization recovery data for all four samples. For  $x=0$  at three different temperatures [193 K (a), 116 K (b), and 30 K (c)]. The dotted lines are the 95% confidence band of the fit. (d) for  $x=0.1$  at 18.3 K ( $\bullet$ ), for  $x=0.5$  at 21.1 K ( $\blacktriangle$ ), and for  $x=1$  at 18.5 K ( $\star$ ). The solid lines are the fit to  $M(\tau) = a + M_0(1 - e^{-\tau/T_1})$ . The open points are not taken into the fitting datasets.

a combination of exponential and stretched exponential growths. Though the nonexponential nature of the magnetization recovery have been mentioned in the literature,<sup>13–15,33,34</sup> except for a few cases,<sup>8,10,18</sup> the  $T_1$ 's were found to fit better to a single exponential model.

The magnetization recovery data for all the samples at different temperatures are shown in Fig. 4. We have tried to fit our magnetization recovery data to a single exponential, a bi-exponential, and a stretched exponential model. In most of the cases, a single exponential fit yields more acceptable statistical results compared to a bi-exponential or stretched exponential fit. The nonexponential nature of the magnetization recovery curve, for the  $x=0$  sample, appears primarily in the initial part of the magnetization recovery, and again at low temperatures when the relaxation time is long. A stretched exponential fit to the magnetization recovery yielded different values for the exponent at different temperatures ranging from 0.9 (at 193 K) to 0.6 (at 30 K) without any specific trend. In some other glass systems it has been found that the exponent is independent of temperature.<sup>18</sup> At 30 mol% of the alkali content the binary alkali borate glasses contain almost 30% of four coordinated boron units along with three coordinated boron units.<sup>12</sup> In the case of a noticeable spectral inhomogeneity, the presence of these two groups of boron nuclei would have given rise to a bi-exponential recovery of the magnetization curve. The fast relaxing component of  $T_1$  obtained from a bi-exponential fit to the magnetization recovery showed a larger error compared to the slow relaxing one which also has values close to that obtained from the single exponential fit. The width of the 95% confidence band is more for both the stretched and bi-exponential models in comparison to the single exponential model. Since the initial nonexponential nature could not be accounted by a stretched or bi-exponential model, we have carried out a single expo-

ponential fit to our magnetization data neglecting a few initial points. This procedure yielded the best possible statistical results in our analysis. A nonexponential nature in the initial part of the magnetization recovery for  $^{11}\text{B}$  has also been reported in ionic glassy conductors, which were attributed to the spin diffusion effect.<sup>34</sup> In some cases, we could not saturate roughly 10% of the equilibrium magnetization, which contributed a dc offset to the magnetization values at different delays. Such difficulties in saturating the NMR signal in borate glasses have been reported previously.<sup>33</sup> It appears that in the present case, the mentioned nature may be due to a fast unsaturated initial magnetization. We have proceeded with single exponential fit to evaluate  $T_1$ . In the case of the doped glasses, the magnetization recovery for  $x=0.5$  and 1.0 remains single exponential for the temperatures studied, while for the  $x=0.1$  sample we found a nonexponential nature in the initial part of the magnetization recovery at low temperatures. We have tried to fit our magnetization recovery data with a model that consists of the combination of single exponential and stretched exponential.<sup>10</sup> The fit statistics, for these doped samples, clearly indicate the model as “over-parametrized” at all temperatures indicating that the contribution from the nondiffusive region is negligible. So, in the case of long  $T_1$  for the  $x=0$  sample, we have again resorted to the single exponential fitting neglecting the initial portion of the magnetization recovery. However, our preliminary measurements on a similar lithium-borate glass clearly shows a bi-exponential recovery of the magnetization. The details of these results will be published shortly.

## V. CONCLUSIONS

From our investigations it appears that for the doped and undoped glasses, studied here, the  $^{11}\text{B}$  nuclear magnetization growth curves fit better to a single exponential equation. The consistency of fitting parameters shown in Table I is also indicative of the fact that single exponential model is appropriate for the magnetization recovery in the glass systems studied. For the doped glasses the NSLR could be explained due to the relaxation through the paramagnetic center (RE ions) in the temperature range studied. The crystal field splitting ( $\Delta$ ) obtained from the  $T_1$  data is found to be independent of the RE impurity concentration. The results also indicate that the impurity concentration upto 1 mol% is too dilute to give rise to a RE-RE interaction and therefore to modify the host glass structure. So, RE ions, in this concentration range, can be regarded as a noninterfering probe to find out the local structure and symmetry of the host glass. From the  $T_1$  data we were also able to extract the diffusion coefficient ( $D$ ) and its values is found to be orders of magnitude smaller than in the corresponding crystalline material. Finally we find that the  $T_1$  data (Fig. 3) increasingly deviates from the used model at low temperatures which warrant further investigations.

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