

¹¹B NMR spin-lattice relaxation study in Nd³⁺-doped binary alkali borate glasses: A possible method to look at the environment of rare-earth sites in glasses

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Rare-earth (RE) doped glasses are widely used for laser and optoelectronic applications and their optical properties depend on the host glass matrix to a large extent. RE doped alkali borate glasses are interesting to observe the effect of network modifiers on the RE environment. In spite of several studies on RE doped glasses, a consensus on the RE environment is still elusive. In this communication we are able to show the effect of the modifier ion on the RE environment in $30R_2O-69.5B_2O_3-0.5Nd_2O_3$ ($R=Li, Na, K, Rb$ and the composition is in mol %) by measuring ¹¹B Nuclear Spin Lattice (NSLR) time over a temperature range 100–4.2 K. These measurements allow us to evaluate the crystal field splitting (Δ) of the two lowest lying multiplets of the ground state ($4I_{9/2}$) of Nd³⁺. We show here that a systematic variation of Δ with the type of alkali can be correlated to the findings from optical and EXAFS measurements. Our results suggest that the next nearest neighbour of RE is the modifier ion itself. We also show that this method has a potential in probing the Medium Range Order (MRO) in glasses which is otherwise difficult to probe by optical or EXAFS measurements.

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I. INTRODUCTION

Over the past four decades several techniques like Fluorescence-Line-Narrowing (FLN),¹⁻⁹ UV-VIS spectroscopy,¹⁰⁻¹² EXAFS,¹³ and also simulation¹⁴ have been used to study the local environment of the RE ions in glasses. However, issues like the extent and origin of variation of the RE environment from site to site, the effect of network modifier on the RE environment or existence of MRO/clustering are not resolved beyond controversy. FLN spectroscopy has contributed mainly to the understanding of the RE environment while UV-VIS and EXAFS studies give only the average properties of the RE environment. However, recent NMR studies¹⁵ in RE doped alkali silicate glasses have indicated the presence of RE clustering over a few nm length scale.

In a previous report¹⁶ we have established the relaxation mechanism in RE doped borate glasses at low temperatures. In this communication we show that the RE environment in glasses can be probed by using ¹¹B NSLR time (T_1) measurements in Nd³⁺ doped binary alkali borate glasses with general formula $30R_2O-69.5B_2O_3-0.5Nd_2O_3$ ($R=Li, Na, K, Rb$ and the composition is in mol % in the temperature range 100–4.2 K, and the measurements yield an experimental verification of some of the proposed effects of network modifier in the RE environment, like reduction of the disorder in the RE environment on increasing the modifier ion mass⁵ and reducing crystal field (CF) splitting^{4,7} or the effect of the electrochemical properties of modifier ions on the RE-O covalency.¹⁴ It also hints the possibility of using this method to probe the structure beyond the short range order found in glasses. Moreover, being a measurement of dynamical property at low temperature, this work adds further information on the RE dynamics in the presence of tunneling modes in the glass.

II. THEORY

It has been found that in RE doped glasses for both dipolar¹⁷ and quadrupolar¹⁶ nuclei the relaxation is through the paramagnetic centers. In crystals, the relaxation of dipolar nuclei by irreversible spin diffusion to the paramagnetic impurities is well established¹⁸ and this also applies to the relaxation in glasses with low to moderate concentration of paramagnetic impurities. The temperature dependence of the T_1 follows the temperature dependence of the electron correlation (relaxation) time (τ_e), assuming that the paramagnetic ion concentration is low enough to neglect the interactions among themselves. For our samples at low temperatures [when $\tau_e \sim T_2$, known as diffusion limited region (DL), see Fig. 1] the SLR time is given by¹⁸

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

Here, C is given by

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

and, D is the diffusion coefficient of the nuclear spin, n_s is the concentration of the impurity, ω_0 is the nuclear Larmor frequency, and τ_e is the electron relaxation (correlation) time. γ_S and γ_I are the gyromagnetic ratios of electronic and nuclear spins respectively, and S is the electron spin quantum number. The electrons in our system relax through Orbach process,¹⁹ i.e., $\tau_e = C_O [\exp(\Delta/k_B T) - 1] / \Delta^3$, where C_O is the relaxation constant for the Orbach process and Δ is the CF splitting of the two lowest multiplets of the Nd³⁺ ground state ($4I_{9/2}$).

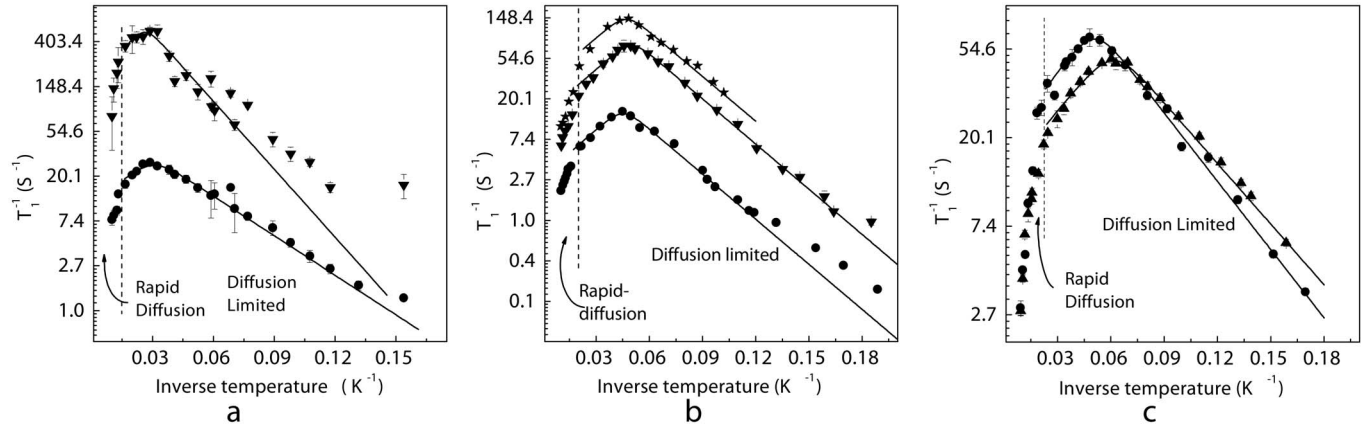


FIG. 1. ^{11}B T_1^{-1} vs T^{-1} plot for the LB, NB, KB, and RB glasses. (a) LB: \blacktriangledown is for long T_1^{-1} , \bullet is for short T_1^{-1} ; (b) NB: \bullet for $x=0.1$, \blacktriangledown for $x=0.5$, and \star for $x=1$ (Ref. 16); (c) KB (\bullet) and RB (\blacktriangle). The solid line is the fit to Eq. (1).

III. EXPERIMENT

The samples were prepared by melting the appropriate amount of corresponding alkali carbonate, boric acid, and RE oxide around 850–900 °C for 30 min, and then quenching them on a brass plate. All the samples were optically homogeneous and their amorphous nature was confirmed by x-ray powder diffraction. The T_1 measurements were done using a homebuilt pulsed NMR spectrometer at 26.04 MHz between 100–4.2 K. A saturation burst pulse sequence was used, comprising of 100–150 $\pi/2$ preparation pulses, followed by another $\pi/2$ monitoring pulse. Typical $\pi/2$ pulse width is 3–4 μs . Details of the experimental procedure are described in our previous report.¹⁶

IV. RESULTS AND DISCUSSION

In our previous report,¹⁶ we have shown that the ^{11}B nuclear magnetization in NB glass (refer to Table I for the nomenclature of the samples) with different RE concentrations follows a single exponential recovery, and fitting the T_1 – T data to Eq. (1) yields a single Δ value. In the present work we found a similar behavior of magnetization recovery for the KB and RB glasses, while the LB glass showed a biexponential magnetization recovery resulting in two Δ values. The fit parameters corresponding to long relaxation rate of LB (henceforth referred as long components) and those corresponding to short relaxation rate values (henceforth referred as short components) along with those for other samples (with $x=0.5$) are listed in Table I. Figure 1 shows the variation of T_1^{-1} with T^{-1} for different alkali borate glasses. We found that the electron relaxes in all samples by Orbach process, in the temperature range studied. This enables us to find the value of Δ within a 10% accuracy. This appears to be the only method to measure the Δ of the two lowest lying multiplets of RE ion directly, since ESR experiments on the RE doped glasses cannot be done due to very fast relaxation time and very broad ESR signal.

It is surprising that we do not observe any significant spread in the Δ values (amounts to a distribution in τ_e) as anticipated from optical experiments. Similar observations have been reported in our previous report¹⁶ and in RE doped

meta-phosphate glasses.¹⁷ In the optical experiments transitions from the higher J multiplets to the lower J multiplets are probed, and information on the Stark splittings, and their distribution is inferred by deconvolving the observed spectra.¹ Earlier reports on FLN spectroscopy (for example, Ref. 2) indicated a continuous variation of the site to site distortion around an average symmetry. But in more recent reports on many Eu^{3+} doped glasses like germanate glass,⁶ fluorozirconate glass,⁸ and sodium borosilicate glass,⁹ it has been found that there are rather well defined multiple RE sites, instead of a large continuous gaussian variation of the site to site distortion. The inhomogeneous linewidths reported by these authors are considerably less than those suggested by the UV-VIS spectroscopy. However, recently Hehlen *et al.*,¹¹ have shown in Er^{3+} doped soda-lime and aluminosilicate glasses that the inhomogeneous broadening due to site to site variation of the crystal field from the

TABLE I. Values of the fitting parameters for different binary borate glasses. $D' = n_s \times D^{3/4}$ [see Eq. (1)]. Δ in K (1 K $\equiv 0.69503 \text{ cm}^{-1}$), D' in $3.7 \times 10^9 (\text{m}^2 \text{ s})^{-3/4}$, C_0 in 10^{-5} s K^3 , and n_s in 10^{26} m^{-3} .

Alkali		Parameters	R^2 of fit	n_s
Lithium (LB)	Long	$\Delta=202(21)$	0.940	2.4
		$D'=167(8)$		
	$C_0=26(10)$			
	Short	$\Delta=118(5)$		
$D'=8.6(2)$				
Sodium (NB)	$\Delta=149(5)$	0.994	2.1	
	$D'=24.9(4)$			
	$C_0=1.2(2)$			
Potassium (KB)	$\Delta=103(3)$	0.995	1.8	
	$D'=20.5(3)$			
	$C_0=3.6(4)$			
Rubidium (RB)	$\Delta=92(3)$	0.989	1.6	
	$D'=16.1(3)$			
	$C_0=1.7(2)$			

$^4I_{15/2} \leftrightarrow ^4I_{13/2}$ optical transition is significantly smaller than the overall crystal field splitting of those multiplets.

Interpretation of the FLN spectra of Nd^{3+} doped glasses is more difficult, due to the presence of five multiplets in the terminal level $4I_{9/2}$ and hence less studied as compared to Eu^{3+} doped glasses. Brecher *et al.*⁴ have reported FLN studies on several Nd^{3+} doped glasses. None of their FLN spectra showed extreme line narrowing, which they attributed to residual inhomogeneous broadening. It has been pointed out that for Nd^{3+} , upper $4I_{9/2}$ multiplets have substantial homogeneous broadening.¹ However, the effect of homogeneous broadening would not be seen in our measurements as the τ_e for all our system is slow enough compared to the typical homogeneous linewidth of RE ground state multiplets. J mixing is expected to have a significant contribution to the optically measured inhomogeneous linewidth by shifting the barycenters of the ground state of the RE ion are probably less effected by these sources of inhomogeneous broadening, while higher J manifold are affected considerably. However, ^{11}B relaxation through particular RE sites with the same Δ is ruled out as in our previous report,¹⁶ we have already shown that for Na- borate glasses with different Nd^{3+} concentrations the D' varies linearly with the concentration of RE ions. This indicates that all of the RE ions take part in the relaxation of boron nuclei.

Our present experimental results of the crystal field splitting of the lowest two multiplets on these systems suggest that in LB glass, the RE ion has two types of sites while for other glasses, there is only one type of site. Figure 2(b) shows the variation of Δ with the alkali mass number (top x -axis) for our systems. From NB to RB it decreases monotonically. For LB, out of the two Δ s the long- Δ follows a general trend of decreasing with increasing mass of the modifier ions, while the short- Δ does not follow this trend. However, if the average value of these two Δ values is taken, it would follow again the same trend with the alkali mass. Figure 2(a) shows the UV-VIS absorption spectra of our samples for the hypersensitive transition ($^4I_{9/2} \leftrightarrow 4G_{9/2}, 2G_{7/2}$), which is most sensitive to the local surroundings of the RE ions. The deconvolution of the absorption spectra shows more distinguishable peaks as the mass of the modifier ion is increased. It is now well known (for example, Ref. 5), that the network modifier ions play more important role on the RE environment than the network former, and heavier the modifier ion, lesser would be the structural disorder in the RE environment. The UV-VIS spectra of our samples also reveal similar trend. There is another interesting aspect of the dependence of the surroundings of the RE ions resulting in the inhomogeneous broadening of FLN/UV-VIS spectra in glasses. It has been observed for Eu^{3+} (Ref. 7) and Nd^{3+} (Ref. 4) that when the glassformer is fluorine the FLN spectra is more well resolved as compared to the oxide glasses. This is attributed to a lesser crystal field splitting, due to the smaller charge on fluorine ligands, in fluoride glasses. Our crystal field measurements clearly correlate these two facts in borate glasses and it can be concluded that heavier alkali atoms produce lesser crystal fields and reduce disorder in the RE environment. Still the question remains, whether the size or electrochemical properties of

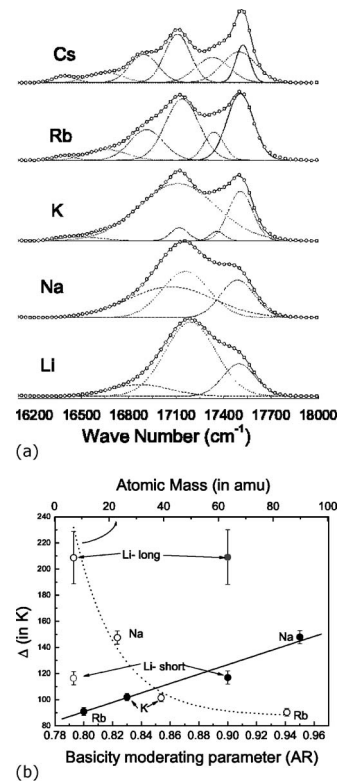


FIG. 2. (a) Absorption spectra for hypersensitive transition in $30\text{R}_2\text{O}-69.5\text{B}_2\text{O}_3-0.5\text{Nd}_2\text{O}_3$ glasses ($\text{R}=\text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$). (b) Variation of Δ with alkali mass number (top x -axis, and \circ) and with basicity moderating parameter (AR) (bottom x -axis, and \bullet). The dotted line is a guide to the eye and the solid line is a linear fit to the Δ values.

the alkali plays the role in influencing the RE environment. In LB, the long- Δ has an unusually high value, as compared to other three glasses and meta-phosphate glasses.¹⁷ One possible reason is that in LB the RE ions belonging to the long- Δ value, have a different environment with higher anionic charge density, which give rise to a higher Δ . This unusual situation may occur if these RE sites coordinate with nonbridging oxygens (NBO) which have a higher charge density and would give rise to higher Δ value (than the short- Δ sites). The RE ions, corresponding to the region of short- Δ , as in other 3 glasses, probably coordinate to charged BO_4 tetrahedra, and would have a smaller Δ .

Existence of alkali rich and alkali poor regions in borate glasses are postulated²⁰ on the basis of IR and far-IR²¹ and dielectric spectroscopy²² by monitoring the motion of the alkali ions and also by molecular dynamics simulations.²³ The smaller the alkali ion size, the larger is the structural inhomogeneity. This seems to be the reason behind the origin of two different types of RE sites in LB glass. It is widely believed that RE ions in glasses prefer 8 coordination with a distorted C_{2v} symmetry, but 6 coordination is also possible.^{13,24} In the alkali-rich region the RE ion would coordinate to NBOs in 6 coordination, which will give rise to a higher Δ . Probably this type of RE coordination has a much larger disorder in the RE environment, as is evident from a larger error bar for this Δ value obtained from our experiment (note that the error bar sufficiently accounts for the

deviation from the model seen in the T_1 vs T data for this case). This is consistent with the general observation in the RE doped glasses that a higher crystal field splitting is associated with a larger disorder in the RE environment. Merging of the two Δ s to one Δ with increasing size of the modifier ions confirms that the homogeneity in the glass increases with increase in size of the modifier ions resulting in only one type of RE environment, which is 8 coordinated. This would also imply that the average coordination number of RE ions would increase with increasing alkali size. Indeed, similar trend has been observed in the EXAFS study in Er^{3+} doped $30R_2\text{O}-70\text{B}_2\text{O}_3$ (for $R=\text{Li, Na, K}$) glasses.¹³ The 8 coordinated RE sites should have a higher covalency in the RE-O bond, as it coordinates to charged BO_4 tetrahedra. This should result in increasing the first Judd-Ofelt parameter (Ω_2) which qualitatively describes the average covalency in the RE-O bond. This has been indeed observed for Nd^{3+} doped $30R_2\text{O}-70\text{B}_2\text{O}_3$ (for $R=\text{Li, Na, K}$) glasses.¹⁰ It should be pointed out that we had reported the observation of a slight non exponential nature in the magnetization recovery in Na-borate glasses, particularly for long T_1 values. This may be due to the presence of a few 6 coordinated sites in Na-borate glasses.

Contrary to the RE doped alkali silicate glasses, the type of second nearest neighbor of RE ions in alkali borate glasses is not resolved in EXAFS studies. In the present study, the variation of Δ with the type of alkali probably affects the charge distribution around the RE ions, suggesting that the alkali ions are the second nearest neighbors in borate glasses also. The Δ values of our glasses are plotted against the basicity moderating parameter²⁵ according to the most popular Allred Rochow scale of electronegativity in Fig. 2(b). The systematic variation of Δ of the 8 coordinated RE ions probably arise due to diminishing electronegativity of the modifier cations. This situation does not arise for the RE ions sitting in the alkali rich regions due to the formation of local NBOs. This indicates that the electrochemical properties of the modifier ions play a major role in the RE environment.

Although the basic emphasis is to understand the change in the RE environment with change in the type of alkali, our measurement can throw some light on the medium range order in these systems, particularly in LB glass. MRO exists in glasses through different length scale.²⁶ In borate glasses, MRO within the length scale of 5 Å up to 10 Å, like the different borate group formation is well studied. Room temperature NMR measurements have revealed the information on the connectivities in the Q_n species and the chain length in certain phosphate and silicate glasses.^{27,28} Sen *et al.* used NMR to identify the clustering of RE ions in certain RE doped silicate glasses.^{15,29} MRO up to a length scale of 50 Å has been widely studied using small angle x-ray and neutron scattering techniques (SAXS and SANS) experiments. However, there is a growing opinion that the most prominent feature of the MRO which is revealed by these small angle scattering experiments, first sharp diffraction peak, comes from some ordered structure of voids or by a ring structure or by a skeleton of heavy atoms surrounding an ordering of light atoms.^{30,31}

Our measurements allow us to obtain one more dynamical quantity of the system, the spin diffusion coefficient for the

^{11}B nuclei (presented here as the product $n_s \times D^{3/4}$), where n_s is calculated from measured density of glasses (Table I). For the samples with single exponential magnetization recovery one can find a unique diffusion coefficient for the whole sample, and this turns out to be of the same order of magnitude for the NB, KB, and RB. For LB glass it cannot be obtained conclusively from these measurements, as the RE site distribution in alkali rich and poor regions is not known *a priori*. It has been anticipated that the RE ion would prefer a position near to the alkali ions, as the network near a modifier site will be highly discontinuous and it would be easier for the RE ion to satisfy its valence requirements although very few experimental verifications are available to support this view.¹⁵

The quantity, D' , in the case of LB glass reveals some information on the clustering of RE ions. One can notice the D' for Li-long is one order of magnitude higher than that for the Li-short. It is reasonable to assume that in the glass, B—O network is distributed homogeneously. So on an average, the B—B distance will not be very different in the Li-rich and Li-poor area. In that case, the spin diffusion coefficient, D , of the ^{11}B nuclei will not differ drastically in the two regions. This naturally implies that, in the Li-rich region the number density of Nd^{3+} ions is one order of magnitude higher than that in Li-poor region. Using this information along with the average ratio of the magnetization corresponding to the ^{11}B nuclei in the Li-rich and Li-poor region, we compare here the average Nd—Nd distance in the Li-rich and Li-poor regions in an order of magnitude calculation. For NB, KB and RB glasses the average radius, r , up to which the spin diffusion operates is given by, $\frac{4}{3}\pi r^3 \times n_s = 1$. The linear scaling of D' with the mol % of Nd_2O_3 in NB glass [Fig. 1(b) or Ref. 16], justifies this assumption for the glasses where the Nd^{3+} is homogeneously distributed. This turns out to be 10.5 Å, 11.1 Å, and 11.4 Å for NB, KB, and RB glasses, respectively. For LB glass, the number density of Nd^{3+} ions in Li-rich region is ~ 20 times more than that in the Li-poor region. Using the average number density of Nd^{3+} ions, obtained from the density of LB glass, we get the number density of Nd^{3+} ions in Li-rich region as $2.4 \times 10^{20}/\text{cm}^3$ and that in the Li-poor region as $1.2 \times 10^{19}/\text{cm}^3$. This can not be used to calculate the Nd—Nd distance, as they are not homogeneously distributed. But it can be reasonably assumed that the Nd ions within the Li-rich region and Li-poor region are themselves homogeneously distributed. If we assume that the ^{11}B nuclei are distributed homogeneously in the glass, the saturation magnetization values corresponding to the short and long relaxation rate in LB glass, would give information about the ratio of the volume occupied by the Li-rich and Li-poor region. We have taken the average of the ratios of these saturation magnetization values for 14 data points near the minima of the relaxation rates. We have excluded the points which are close to the rapid diffusion regime or at very low temperatures. The average value of the ratio is 0.5(1), indicating that in a unit volume about 1/3 of the ^{11}B are relaxed by Nd ions which are in the Li-rich region and 2/3 by those in the Li-poor region. Using this fact, we get the diffusion radius for Nd^{3+} ion in the Li-rich region is ~ 7 Å, while that in Li-poor region is ~ 24 Å. So, the minimum radius of the Li-rich re-

gion, which can accommodate 20 Nd³⁺ ions, is ~ 2 nm. We would like to point out that, the magnetization ratio we presented here is only a rough estimate, as in some cases there was an initial unsaturated magnetization.

To support our proposition, we have carried out preliminary ⁷Li T_1 measurements in 30 Li₂O-(69-x)B₂O₃-xNd₂O₃ glasses at room temperature. These results also seem to indicate the presence of Li-rich and Li-poor regions in these glasses. The measurements were done at room temperature in Bruker DSX300 spectrometer with an inversion recovery sequence, with a $\pi/2$ pulse-width of 4.2 μ s at 116.59 MHz. The magnetization recovery for $x=0.5$ sample is double exponential with the longer $T_1=757(17)$ ms and the shorter $T_1=75(9)$ ms; the ratio being 10. The relaxation mechanism probably is in the rapid diffusion regime, as the temperature is high enough to ensure $\tau_e \ll T_2$. In the rapid diffusion case, for a dipolar nucleus T_1^{-1} is given by,¹⁸

$$\frac{1}{T_1} = \frac{4\pi}{3} \frac{n_s \gamma_I^{3/2}}{(\gamma_I \gamma_S \hbar)^{3/2} S^{3/2}} C \left(\frac{\Delta\omega}{\omega_0} \right)^{3/4} \left(\frac{k_B T}{3a_0} \right)^{3/4}, \quad (3)$$

where, a_0 is the inter nuclear spacing, $\Delta\omega$ is the intrinsic linewidth of the nuclei, and C is given by Eq. (2). T_1^{-1} is still proportional to number density of the paramagnetic impurities in the rapid diffusion regime. This somewhat lower ratio as compared to the ratio we got from the ¹¹B relaxation rate measurements is not unusual, as the number of relaxing Li ions in the Li-rich region is also higher. For $x=0$, the magnetization recovery follows a stretched exponential function of the form $M(\tau) = M_0 [1 - a \exp(-(\tau/T_1)^n)]$, with $T_1 = 1733(70)$ ms, and $n=0.72(4)$. The stretched exponential behaviour may arise due to the presence of Li clusters. Moreover, T_1 measurement in $x=0$ sample indicates that for $x=0.5$ sample the relaxation is mainly through paramagnetic impurities. Details of these measurements for different values of x will be published elsewhere.

The diffusion barrier, b_0 , where the spin diffusion does not operate, is given by,

$$b_0 = \left(\frac{\gamma_S^2 \hbar H_0}{\gamma_I 2 k_B T} \right)^{1/4} r_{B-B}, \quad (4)$$

where, H_0 is the resonance field for the ¹¹B nucleus, and r_{B-B} is the average boron-boron distance. To find r_{B-B} we use the average bond length of the B—O bond and the average B—O—B bond angle reported in literature, which are approximately 1.38 Å and 122°, respectively. It can be as-

sumed that r_{B-B} , which turns out to be 2.4 Å, is same for all glasses. However, if calculated from the boron number density, it increases nominally from LB to RB glass. b_0 , for $H_0=1.923$ T, and $T=20$ K is ~ 8 Å. This is clearly in contradiction to the Nd—Nd distance we got for Li-rich region in LB glass. Equation (4) is an approximate equation in the case, where the nuclei maintain the spin temperature by dipole-dipole interaction. The nuclei, which are inside the diffusion barrier see the field produced by the paramagnetic impurity much higher than their intrinsic dipolar width, and hence do not participate in the spin diffusion process. In the present case, the ¹¹B nuclei, particularly which are in the BO₃ groups have a broad line shape due to the distribution of the EFG, which is considerably broader than their intrinsic dipolar linewidth. In the present case, we can say that Eq. (4) gives an overestimated value of b_0 which is not physical. For 30 Na₂O-69 B₂O₃-1 Nd₂O₃, the estimated Nd—Nd distance is ~ 8 Å. We did not observe Nd—Nd interaction in this system.¹⁶

V. CONCLUSION

In conclusion our NMR measurements are able to probe the RE environment and it also opens up a possibility of looking into the MRO in the glass, which is otherwise difficult to probe by optical or EXAFS measurements. The crystal field splitting of the lowest two multiplets of the ground state of Nd³⁺ ion is not sensitive to the slight site to site variation of RE environment in glasses but it shows substantial variation with the host glass composition, which can be used to get information on the RE environment. We have correlated some of the findings of optical and EXAFS experiments with our NMR measurements in these systems as revealed by the systematic variation of the crystal field splitting with the mass of the alkali modifier ions. Our results also indicate that the next nearest neighbor of the RE ion is probably the modifier ion itself. Also until the lowest temperature of our measurement the electronic spin-lattice relaxation (and hence NSLR) is dominated by the Orbach process, and the tunnel modes present in the glasses may become more effective in causing NSLR at still lower temperature.

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