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Nuclear magnetic resonance and ionic motion in fluorozirconate glasses

S. ESTALJI, R. KÜCHLER, O. KANERT, R. BÖLTER, H. JAIN ^{*(1)} and K. L. NGAI^{**}

Institut für Physik, Universität Dortmund, 4600 Dortmund 50, Germany

**Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, U.S.A.*

***Naval Research Laboratory, Washington, DC 20375, U.S.A.*

ABSTRACT

We have determined NMR linewidths and nuclear spin relaxation rates for ^{19}F , ^7Li , and ^{23}Na nuclei, and electrical conductivity in ZrF_4 -based fluoride glasses as a function of temperature. The results indicate that both Li and F are mobile in the glass containing 20 mole% LiF, whereas only F is mobile in glasses containing NaF (up to 30 mole%) or no alkali ions. Finally we compare and discuss the activation energies for the various parameters.

RESUME

Des mesures de conductivité électrique et de RMN de ^{19}F , ^7Li et ^{23}Na ont été réalisées sur des verres fluorures à base de ZrF_4 : les variations des largeurs de raies de resonance et des temps de relaxation ont été étudiées en fonction de la température. Les résultats démontrent que les ions Li et F sont mobiles dans le verre contenant 20% de LiF (en fraction molaire). Dans le cas des verres contenant du NaF (jusqu'à 30% en mole) ou ne contenant pas de cation alcalin, seul l'ion F est mobile. Les énergies d'activation déduites des divers paramètres sont comparées et analysées.

INTRODUCTION

The ZrF_4 -based fluoride glasses were originally reported to be fluoride ion conductors/1/. However, when alkali ions are also present these glasses become mixed cation-anion conductors: the relative contribution of the cations and anions being dependent on the concentration and nature of the alkali ion/2,3/. In this context nuclear magnetic resonance (NMR) techniques have been proven to be very useful, for example, by demonstrating that only a fraction of F contributes to ionic conduction /2,4,5/. At present there are two interesting questions on this subject: (a) how does the F anion movement compare with the alkali movement? (b) Do conductivity and NMR perceive ion movement in the same way? The first question has been addressed in the references mentioned above, but a rigorous answer to the second question has been sought only recently/6/. In this report we present data on six glasses which elucidate these questions further.

EXPERIMENTAL

The experiments were performed on six ZrF_4 -based glasses listed in Table 1. ^{19}F , ^7Li and ^{23}Na nuclear spin relaxation (NSR) rates were measured using a modified Bruker SXP 4-100 coherent pulsed NMR spectrometer. The NSR rates in the laboratory frame, $1/T_1$, were measured by a π - τ - $\pi/2$ pulse

(1) Currently a Humboldt Fellow at Universität Dortmund

sequence, while those in the rotating frame ($1/T_{1\rho}$) were observed by the spin-locking technique. In $T_{1\rho}$ -experiments the value of the spin-locking field B_1 was chosen such that the effective Larmor frequency was 28kHz to 62 kHz. The linewidth for the same three nuclei was determined from the off-resonance free induction decay after Fourier transformation. The electrical conductivity was measured in the frequency range of 10Hz to 100kHz using a 1620 General Radio ac bridge assembly.

Table 1 Composition of fluorozirconate glasses (in mol%)

Glass	ZrF ₄	HfF ₄	BaF ₂	LaF ₃	AlF ₃	LiF	NaF
ZBLALi(II)	50.53	-	21.43	4.44	3.38	20.24	-
ZBLAN(II)	27.43	27.4	19.76	3.06	3.19	-	19.19
ZBLA(II)	59.45	-	30.87	5.69	3.99	-	-
ZBLAN10	59.62	-	22.5	4.5	3.38	-	10
ZBLAN20	53	-	20	4	3	-	20
ZBLAN30	46.37	-	17.5	3.5	2.63	-	30

RESULTS

The temperature dependence of ^{19}F and ^{23}Na linewidths in ZBLAN20, and of ^{19}F and ^7Li linewidths in ZBLALi(II) glasses are shown in Figs.1a,b. For both glasses ^{19}F linewidth shows a sudden decrease upon heating above a particular temperature which represents the onset of motional narrowing when the linewidth becomes comparable with the F jump rate. The temperature dependence of linewidth in the motional narrowing region has been analyzed following Hendrickson and Bray/7/. The best fits to data are shown by the solid lines with the condition from theory that the linewidth approaches zero at sufficiently high temperatures. The activation energies calculated from various motional narrowing data, $E_{\delta\nu}$, are listed in Table 2.

Figs. 1a,1b Linewidth of ^{19}F ($\square$) and ^{23}Na ($\circ$) in ZBLAN 20 (left figure) and of ^{19}F ($\square$) and ^7Li (Δ) in ZBLALi(II) (right figure) as a function of temperature. Solid lines are based on theory/7/.

In this paper we are interested only in the NSR rate due to the ion diffusion which becomes effective for relaxing the spins at about room temperature and above/8/. That is, to obtain diffusion-induced NSR rate the low temperature background contribution are to be subtracted from the total observed NSR rates. The temperature dependences of the so corrected NSR rates are shown in

Fig.2 ^{19}F and ^7Li NSR-rates, $1/T_1\text{Diff}$, in ZBLAlI(II) for Larmor frequencies 15 MHz ($\square$); 251 MHz ($\circ$); 69.5 MHz ($\blacksquare$) Δ denote extrapolated conductivity data (see text)

Fig.3 ^{19}F and ^{23}Na NSR-rates, $1/T_1\text{Diff}$, in ZBLAN(II) for Larmor frequencies 15 MHz ($\square$); 56.5 MHz ($\bullet$); 251 MHz ($\circ$); 70 MHz ($\blacksquare$); $\times$ denote extrapolated conductivity data (see text)

Figs. 2 and 3 for ZBLAlI(II) and ZBLAN(II) glasses, respectively, for various nuclei and Larmor frequencies. Note that the NSR rates increase with temperature in an Arrhenius fashion from which we have obtained respective activation energies (E_{T_1}) as listed in Table 2. The magnitude of the relaxation rates depends on Larmor frequency ω_0 as $\sim \omega_0^{-\beta}$ where $\beta = 1.1 \pm 0.1$. These NSR rates in laboratory frame are obtained at Larmor frequencies which are one or more orders of magnitude higher than the highest frequency of ac conductivity measurements. Therefore, to have a common frequency in the two techniques, NSR rates have been measured in the rotating frame with lower effective frequencies. Results of these measurements on ZBLAN(II) glass are shown in Fig.4 for three different effective frequencies. Note that at such frequencies it has been possible to observe the maximum in NSR rate below the glass transition temperature. The low and high temperature sides of the peak give activation energies $E_{T_1}^{\text{lo}} = (0.26 \pm 0.02)$ eV and $E_{T_1}^{\text{h}} = (0.76 \pm 0.1)$ eV, respectively. Within the experimental error $E_{T_1}^{\text{lo}}$ is the same for all the three frequencies.

Finally, we have obtained dc conductivity σ_{dc} for three glasses using complex impedance analysis. Plots of $\ln(\sigma_{\text{dc}} \cdot T)$ vs $1/T$, where T is the absolute temperature, give the activation energy E_{dc} which is given in Table 2. However, we consider fixed frequency ac conductivity to compare with the NSR rate at the same fixed frequency. This comparison is shown in Fig. 4 where $\sigma_{\text{ac}} \cdot T$ at 30 kHz is plotted vs $1/T$.

DISCUSSION

From Fig. 1 we note that the motional narrowing of ^7Li and ^{19}F occurs in the same temperature range. This is consistent with the previous observations that in ZrF_4 -based glasses containing 20 mole% LiF both Li and F ions contribute to electrical conduction/2,3,5/. In contrast, for the sodium containing glasses ($\text{NaF} = 10$ to 30 mole%) we observe motional narrowing primarily for ^{19}F which should therefore be the predominant mobile species. The ^{23}Na linewidth decreases with increasing temperature but to a much smaller extent; this can be attributed simply to the motion of ^{19}F ions. Thus we conclude that our sodium containing

Fig.4 Temperature dependence of ^{19}F NSR in ZBLAN(II) in the rotating frame, $(1/T_{1\rho})_{\text{Diff}}$, for different effective Larmor frequencies: 28 kHz ($\circ$); 42 kHz ($\bullet$); 62 kHz ($\square$); $\blacksquare$ denote conductivity data at 30 kHz

glasses remain primarily F ion conductors. In our experimental method it has been difficult to resolve the ^{19}F line into that due to mobile and immobile fluorine ions/4/. Nevertheless, the fact that there is a residual ^{19}F linewidth even at the highest temperature suggests that some F atoms never become mobile.

The obvious observation from the data for the first three glasses in Table 2 is that the activation energy for dc conductivity is about 3 times larger than E_{T_1} or E_{δ_V} . This is similar to a common feature found in oxide glasses/9/, and is believed to be a consequence of inter-particle interactions which also manifest as the power law dependence of conductivity on frequency. The values of E_{T_1} at various frequencies and E_{δ_V} are the same for a given glass within experimental error. In fact, we obtain the same activation energy $E_{\text{disp}}^{\text{ac}}$ for fixed frequency ac conductivity in the range of tens of MHz. For that we extrapolated conductivity data taken in the region between 10Hz and 100kHz to the corresponding NMR Larmor frequencies (see Table 2). Therefore we conclude that for these three glasses both the NMR and ac conductivity are in the same dispersive region (where $\sigma \sim \omega^s$, s is a constant) of ion jump phenomenon/10/. At present for the last two glasses in Table 2 we do not have E_{dc} data but we expect it to be comparable to the values for the first three glasses. Then we note that E_{δ_V} is similar in magnitude to E_{dc} than to E_{T_1} . Clearly, in these glasses the linewidth experiment is conducted in a different frequency region than the T_1 -experiment. The former should be in or around the Gaussian region (where σ is frequency independent) whereas the latter continues to be in the dispersive region. It has been implicit in the above discussion that NMR and conductivity experiments perceive ion movement in the same way, the observed difference between the activation energies for the two phenomena is obviously caused by the different frequencies in the two experiments. Figure 4 offers a verification of this assumption. Here we note that under the conditions of identical frequencies E_{ac} seems to be equal to E_{T_1} but only in a limited temperature region (below 400K; see dashed line in Fig.4). At higher temperature E_{ac} approaches E_{dc} , whereas E_{T_1} maintains its low value until reaching the maximum. We believe that this discrepancy occurs because σ_{ac} encounters the Gaussian region of the frequency spectrum at a lower temperature than $1/T_{1\rho}$. Of course, on the high temperature side of the peak in figure 4 both σ_{ac} and $1/T_{1\rho}$ are in the Gaussian region and the two have the same slope equal to E_{dc} . Thus we conclude that, in principle, NSR and conductivity depend on the same kind of ion movement but it is not necessary for the two phenomena to cross from dispersive to Gaussian regions at the same frequency.

Table 2 Activation energies (in eV) for the six investigated glasses as calculated from nuclear spin relaxation and linewidth measurements for different nuclei and at different Larmor frequencies and activation energies from conductivity experiments.

Glass	NMR							conductivity	
	<u>Nuclear spin relaxation</u>						<u>linewidth</u>		
	⁷ Li		¹⁹ F			²³ Na	⁷ Li ¹⁹ F		
	23 MHz	69 MHz	15 MHz	56 MHz	251 MHz	70 MHz	⁷ Li ¹⁹ F	E _{dc}	E _{ac} ^{disp.}
	E _{T1}	E _{T1}	E _{T1}	E _{T1}	E _{T1}	E _{T1}	E _{δv} E _{δv}		
ZBLALi(II)	0.28	0.27	0.27	0.28	0.31	-	0.3 0.26	0.89	0.29
ZBLAN(II)			0.27	0.28	0.28	0.3	- -	0.89	0.29
ZBLA(II)			0.25	0.26	0.25	-	- -	0.75	0.26
ZBLAN 10			0.24	0.24	-	-	- -	-	-
ZBLAN 20			0.24	0.24	-	-	- 0.73	-	-
ZBLAN 30			0.24	0.24	-	-	- 0.74	-	-

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