

Alkali Fluoride Containing Fluorozirconate Glasses: Electrical Properties and NMR Investigation

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Electrical properties of glasses inside the ZrF_4 - BaF_2 - ThF_4 - LiF system have been studied as a function of composition by conductivity and NMR measurements. Two series of materials can be distinguished. The transport properties of highly concentrated Li^+ glasses seem only to result from the Li^+ concentration and to increase with that concentration. On the contrary, a mixed contribution of F^- and Li^+ ions must be considered for the low Li^+ concentration glasses. On the other hand, the modifier cations (Ba^{2+} at low concentrations of lithium, Li^+ at high ones) can greatly influence the transport properties. Glasses with a high Li content exhibit good electrical performance (e.g., $\sigma_{175^\circ C} \approx 2 \times 10^{-4} \Omega^{-1} cm^{-1}$ for the glass of composition $Zr_{0.20}Ba_{0.10}Li_{0.60}Th_{0.10}F_2$). © 1985 Academic Press, Inc.

Introduction

There is increasing interest in fluoride glasses because of their potential use for making infrared optical components and ultra low-loss optical fibers (1-3). More recently, the investigation of the transport properties of some fluoride ternary glasses belonging to systems such as the ZrF_4 - BaF_2 - ThF_4 or ZrF_4 - BaF_2 - LnF_3 , has shown that these materials are also F^- ion conductors (4).

As large amounts of an alkali fluoride can be incorporated in such a ternary glass (5), we have investigated the influence of LiF on the electrical properties of glasses belonging to the ZrF_4 - BaF_2 - ThF_4 system.

Some preliminary work (6, 7) in the Li^+ low concentration domain ($c \approx 20$ mole%), has shown a gradual decrease in the conductivity with Li^+ content and a simultaneous increase of the activation energy; a reduction of the number of carriers due to trapping of Li^+ ions by F^- ions has been suggested (7). The existence of glasses in high Li^+ concentrations (up to 60 mole%) (8) has led us to study the evolution of transport properties for larger amounts of LiF . As a matter of fact, one could hope that Li^+ ions themselves become mobile, with increasing Li^+ content. An NMR study, pursued simultaneously, would permit the determination of the nature and the number of carriers with composition of glasses of the ZrF_4 - BaF_2 -

TABLE I
COMPOSITION (mole%), T_G (GLASSY TRANSITION TEMPERATURE), $\sigma_{175^\circ\text{C}}$, AND ΔE FOR
SOME STUDIED GLASSES

Sample	ZrF ₄	BaF ₂	LiF	ThF ₄	Overall composition	T_G (°C)	$\sigma_{175^\circ\text{C}}$ ($\Omega^{-1}\text{cm}^{-1}$)	ΔE (eV)
1	0	10	60	30	MF ₂	280	2×10^{-4}	0.58
2	10	10	60	20	MF ₂	242	2×10^{-4}	0.58
3	20	10	60	10	MF ₂	220	2×10^{-4}	0.54
4	30	15	45	10	MF _{2.35}	232	2×10^{-5}	0.67
5	40	25	25	10	MF _{2.75}	252	2×10^{-7}	0.85
6	50	20	20	10	MF ₃	255	2×10^{-7}	0.91
7	60	15	20	5	MF _{3.10}	262	2×10^{-7}	0.90
8	57.5	33.75	0	8.75	MF _{3.325}	320	2×10^{-6}	0.78

ThF₄-LiF quaternary system and provide substantial information relative to the conduction mechanisms.

Electrical and NMR measurements have been carried out on vitreous samples annealed for some hours below T_G and then slowly cooled. The investigated glass compositions and the glass transition temperatures (T_G) are recorded in Table I.

I. Ionic Conductivity

For all glass samples studied between 20°C and T_G the conductivity values obey the Arrhenius law; activation energies have been calculated using the relation $\sigma = \sigma_0 \exp(-\Delta E/kT)$. Table I specifies the values of σ at 175°C and the activation energy ΔE for the glass compositions considered.

Figure 1 shows the variation of $\log \sigma_{175^\circ\text{C}}$ and ΔE as a function of the Li/F ratio which appeared to be the most representative of the glass composition. A minimum in conductivity corresponding to a maximum of ΔE can be detected when this ratio is equal to about 0.07.

A study of quaternary glasses belonging to the ZrF₄-BaF₂-LaF₃-LiF system (9) has shown that the Li⁺ ions can be considered rather as network formers at low Li⁺ concentrations, and as network modifiers at high concentrations. The transition took place for the value Li/F \approx 0.06, which is very close to the minimum of conductivity.

A. Low Li⁺ Concentration Domain

The comparison of electrical properties of glasses 7 and 8 confirms that introduction of LiF in small amounts into a lithium-free glass decreases the electrical performance. Nevertheless, examination of glasses 5, 6, and 7 in which Li⁺ concentration is approx-

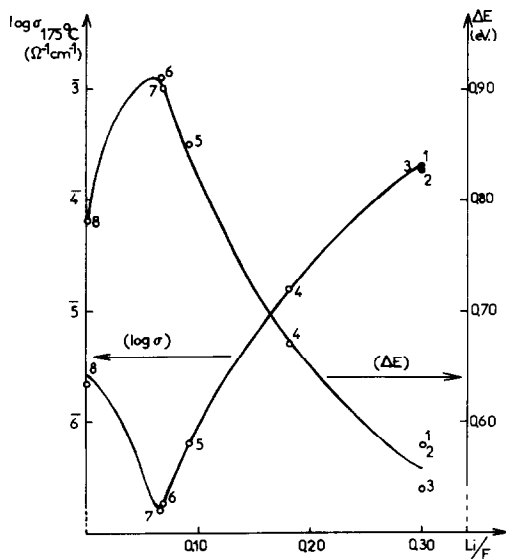


FIG. 1. Variation of $\log \sigma_{175^\circ\text{C}}$ and ΔE as a function of Li/F ratio.

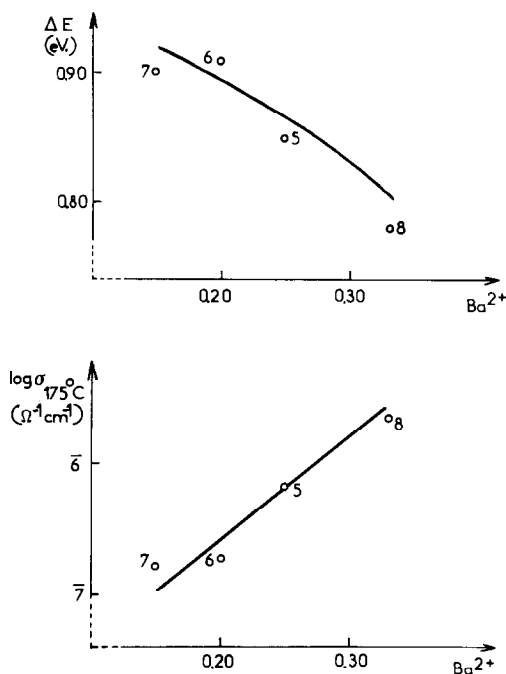


FIG. 2. Variation of $\log \sigma_{175^\circ C}$ and ΔE vs Ba^{2+} concentration.

imately the same and the global compositions of which are respectively $MF_{2.75}$, MF_3 , and $MF_{3.10}$ (M representing all cations present), shows that only a part of the F^- ions are mobile and that this portion is not proportional to the total number of F^- ions present. A follow-up study of these materials by ^{19}F NMR, as shown below, permits one to determine the number of mobile F^- ions.

In this low Li^+ concentration domain the electrical properties seem strongly related to the concentration of the Ba^{2+} modifier cations: as a matter of fact, when the Ba^{2+} concentration increases, the conductivity increases monotonically and the activation energy decreases simultaneously (Fig. 2). An analogous result has been observed with NaF as alkali fluoride (4, 10).

B. High Li^+ Concentration Domain

In this concentration domain $\log \sigma_{175^\circ C}$

and ΔE are quasi-linear functions of the Li^+ concentration, increasing and decreasing, respectively, with increasing Li^+ content (Fig. 3). Consequently, it seems that Li^+ ions are the most mobile carriers in the high Li^+ concentration domain. The following study by 7Li NMR confirms this point.

Glasses such as samples, 1, 2, or 3 which are the first known Li^+ conductor-fluoride glasses, exhibit good conductivities and offer much interest for applications in electrochemical devices.

II. NMR Investigation

The NMR study has been performed on 7Li and ^{19}F nuclei over the temperature range 170–450 K. The magnetic field has been swept by 200 G about the resonance field of 7Li , but only the central part (40 G) is shown in Fig. 4a.

As an example, Figs. 4a and b provide the lithium and fluorine line shapes at various temperatures for glass 2.

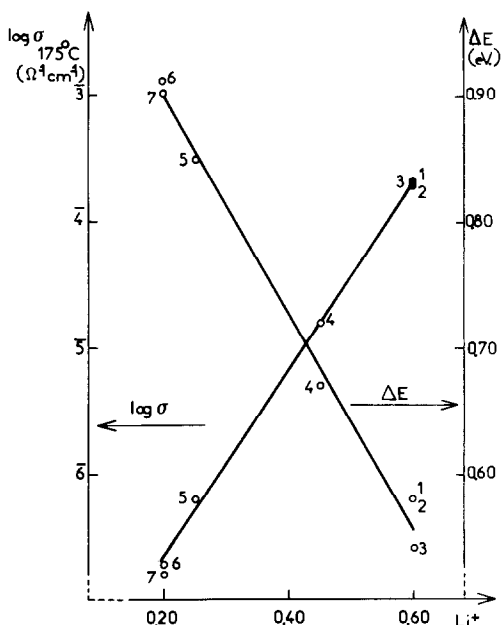


FIG. 3. Variation of $\log \sigma_{175^\circ C}$ and ΔE as a function of the Li^+ concentration.

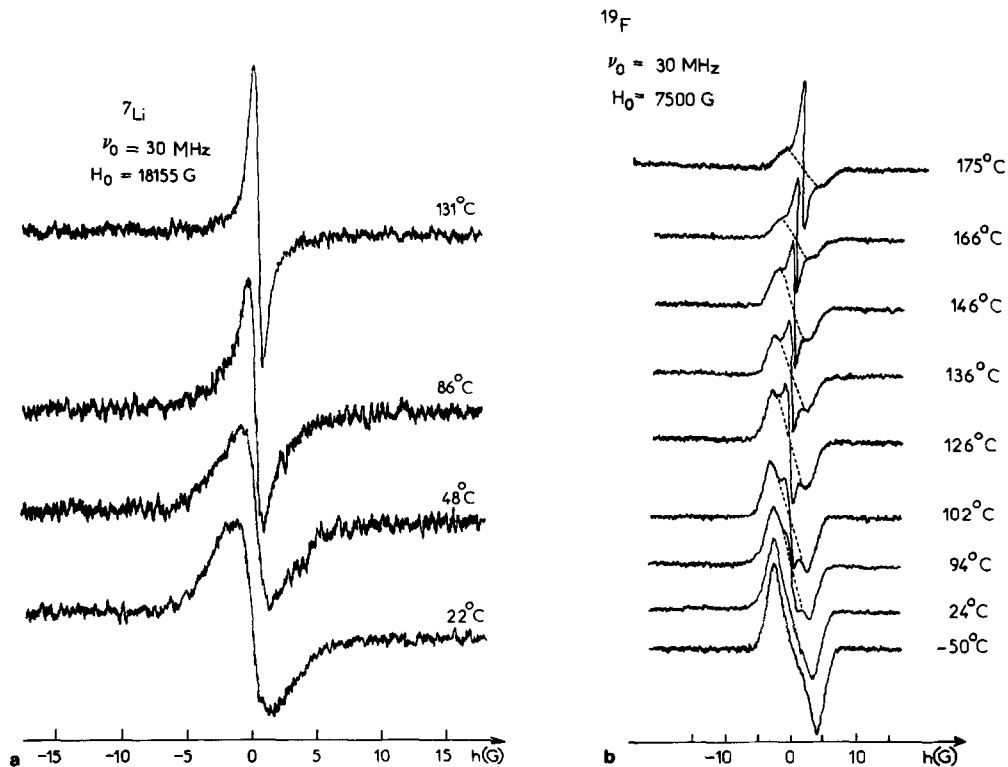


FIG. 4. (a) Thermal variation of the ${}^7\text{Li}$ resonance line (sample 2). (b) Thermal variation of the ${}^{19}\text{F}$ resonance line (sample 2).

No quadrupolar effect is detected in the lithium spectrum; only a narrowing continuous line is observed from T_{ALi} up to the highest experimental temperature (i.e., T_{ALi} , the temperature above which the rigid lattice linewidth $(\Delta H_{\text{pp}})_{\text{Li}}$ decreases). As a consequence, all Li^+ ions appear to be mobile for $T > T_{\text{ALi}}$ (see Table II). The T_{ALi} temperatures of the investigated glasses and the activation energies ΔE_{Li} deduced from the thermal variation of $(\Delta H_{\text{pp}})_{\text{Li}}$ are provided in Table II. The values of ΔE_{Li} are smaller than those obtained by conductivity measurements and are typical of Li^+ local motions.

The thermal change of the fluorine line shape is more complex (Fig. 4b). At low temperature only a broad line can be observed. At increasing temperatures, above T_{AF} , a narrow line characteristic of mobile

F^- ions appears and grows at the expense of the broad line. The extreme limit of narrowing has not yet been reached at the highest experimental temperature just below T_{G} . Consequently, only a part of the F^- ions are mobile at a given temperature, but this number grows with temperature. The T_{AF} temperatures, and the activation energies ΔE_{F} deduced from the thermal variation of $(\Delta H_{\text{pp}})_{\text{F}}$ are listed in Table II for the glasses studied. The values of ΔE_{F} are as weak as those of ΔE_{Li} and characterize the local motions of F^- ions (6).

These results allow us to classify the materials into two groups. The first group is constituted by high LiF concentration glasses (glasses 1, 2, 3, and 4) and is characterized by values of T_{ALi} and ΔE_{Li} lower than those of T_{AF} and ΔE_{F} , respectively. By contrast, the second group which includes

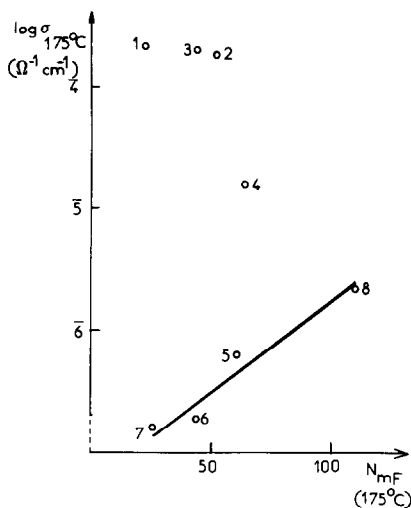


FIG. 5. Variation at 175°C of $\log \sigma$ vs N_{mF} , the number of mobile fluorine atoms.

the low LiF concentration glasses (5, 6, 7, and 8) involves values of T_{ALi} and ΔE_{Li} higher than those of T_{AF} and ΔE_F . The Li⁺ ions are the more mobile in the former group, but the F⁻ ions are more mobile in the latter.

TABLE II

TEMPERATURES T_{ALi} AND T_{AF} ABOVE WHICH Li⁺ AND F⁻ ARE SEEN MOBILE,^a MOTION ACTIVATION ENERGIES OF Li⁺ (ΔE_{Li}) AND F⁻ (ΔE_F), MOBILE FLUORINE FRACTION AT 175°C ($f_{175^\circ C}$) AND NUMBER OF MOBILE FLUORINE IONS FOR A TOTAL NUMBER OF CATIONS EQUAL TO 100 AT 175°C ($N_{mF(175^\circ C)}$)

Sample	T_{ALi} (K)	ΔE_{Li} (eV)	T_{AF} (K)	ΔE_F (eV)	$f_{175^\circ C}$	$N_{mF(175^\circ C)}$
1	255	0.17	353	0.21	0.112	22.4
2	250	0.13	323	0.15	0.260	52
3	258	0.15	293	0.18	0.220	44
4	258	0.16	297	0.17	0.270	63.5
5	285	0.16	273	0.10	0.220	60.5
6	303	0.22	293	0.13	0.145	43.5
7	307	0.19	288	0.10	0.082	25.4
8	—	—	273	0.15	0.330	109.7

^a The mobility of ions is detectable by NMR when the jump frequency ν_s of the mobile ion is of the order of the corresponding low temperature linewidth (expressed in frequency units): for ⁷Li | linewidth: 3.5 G (~5.6 KHz) | $\nu_s > 6$ KHz; for ¹⁹F | linewidth: 8 G (~32 KHz) | $\nu_s > 30$ KHz.

The number of mobile fluoride ions at a given temperature has been determined for each sample from the ratio of the integrated surfaces of the narrow and broad fluorine resonance lines. The mobile fluorine fraction at 175°C, $f_{175^\circ C}$, and the number of mobile fluorine atoms N_{mF} for a total cation number of 100 are given in Table II. Even at high temperature only a small part of the fluorine present is mobile: $f = 0.33$ in the best case, i.e., for sample 8.

Figure 5 depicts the variation at 175°C of $\log \sigma$ versus N_{mF} . The conductivity of glasses belonging to the first group (glasses 1 to 4) is independent of the number of mobile fluorine atoms. The electrical measurements have shown, on the other hand, that in the high LiF concentrated glasses, the transport properties are strongly correlated with the LiF rate (Fig. 3).

By contrast, samples 5, 6, and 7 (second group) show a conductivity simultaneously proportional to lithium concentration and number of mobile fluorine atoms (Figs. 3 and 5). A mixed contribution of Li⁺ and F⁻ ions must be considered for the low LiF content glasses, even when the greater part of mobile ions are F⁻. The lithium-free sam-

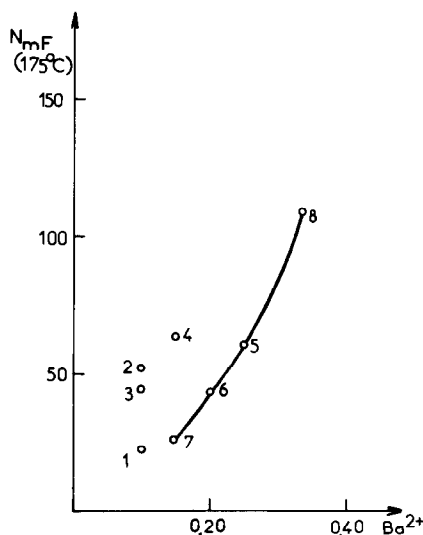


FIG. 6. Variation of N_{mF} at 175°C vs Ba²⁺ concentration.

ple 8 could be included in this second group.

Figure 6 specifies the variation of N_{mF} at 175°C as a function of Ba^{2+} concentration for the low LiF concentration glasses (samples 5 to 8). N_{mF} increases regularly and quickly with Ba^{2+} concentration. This result shows the large influence of the network-modifying Ba^{2+} ions on the transport properties of low LiF concentration glasses.

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