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Elaboration and Ionic Conductivity of New Lithium Fluoride Glasses Prepared from MF_4 Tetrafluorides (M = Zr, Th, U)

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The LiF-based fluoride glasses have been obtained in the LiF-MF_4 (M = Zr, Th, U) binary systems as well as in the ternary LiF–Zr_4–ThF_4, LiF–ZrF_4–UF_4, and LiF–ThF_4–UF_4 systems by a "splat roller quenching" technique. The LiF content can attain 85% (mole). Various properties, including chemical durability, thermal behavior, and ionic conductivity, have been determined. Glasses with high Li content have a high electrical conductivity (e.g., $\sigma_{120°C} \simeq 5.10^{-4}\ \Omega^{-1}\ cm^{-1}$ for $Li_{0.80}U_{0.20}F_{1.60}$).

Introduction

Materials with high Li^+ ion conductivity have been extensively studied in the last decade because of the high voltage and mass energy expected for lithium batteries (*1–9*). Much attention has been focused on lithium glasses because they present some technological advantages, for instance, composition flexibility, lack of defects at grain boundaries, workability, and convenient deposition as thin layers (*10–16*). Lithium fluoride glasses have a special interest due to their good electrochemical stability which results from the high free energy of the fluorides and the strong electronegativity of fluorine (*17*). These criteria can be extended to fluoride thin films. Recently evaporated LiF thin films containing divalent or trivalent metal fluorides have been prepared and their electrical conductivity determined (*18–20*). Samples containing either NiF_2 or AlF_3 have a good conductivity (e.g., $\sigma_{120°C} \simeq 10^{-4}\ \Omega^{-1}\ cm^{-1}$ for $Li_{0.82}Ni_{0.18}F_{1.18}$ and $Li_{0.84}Al_{0.16}F_{1.32}$).

ZrF_4- and HfF_4-based fluoride glasses have been widely studied in the past 10 years because of their potential ability for constituting IR transparent optical components (e.g., ultra low-loss optical fibers (*21–23*). On the contrary, the investigation of the transport properties of those materials has begun only recently. A study of some fluoride ternary glasses belonging to systems such as ZrF_4–BaF_2–ThF_4 or ZrF_4–BaF_2–LnF_3 has shown that these materials are F^- ion conductors (*24–28*). On the other hand the existence of glasses containing large amounts of LiF (up to 60%) within the LiF_4–ZrF_4–BaF_2–ThF_4 quaternary system (*29*) has allowed some of us to determine in a previous work the variation of the

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transport properties with LiF content (*30*). A minimum of ionic conductivity associated with a maximum of activation energy has been detected when the Li/F ratio is equal to ≈ 0.07. In the lower Li concentration domain σ increases regularly and ΔE decreases simultaneously when the BaF_2 concentration increases; on the contrary in the higher Li concentration region, log σ and ΔE are quasi-linear functions, increasing and decreasing, respectively, with LiF rate. A ^7Li and ^{19}F NMR investigation has shown that Li^+ and F^- ions are actually simultaneously mobile and the temperature dependence of the number of mobile F^- ions has been determined. In the low Li concentration domain transport properties result from mixed contributions of mobile Li^+ and F^- ions; for high Li concentrations they depend only on the Li^+ rate. Glasses with high Li content have a good electrical behavior (e.g., $\sigma_{120°C} \simeq 5.10^{-5}\ \Omega^{-1}\ cm^{-1}$ for $Li_{0.60}Zr_{0.20}Ba_{0.10}Th_{0.10}F_2$).

One may conclude that even better electrical conductivity could be expected for materials with LiF amounts higher than 60%. Such a prediction led us to prepare LiF-rich glasses within the LiF–MF_4 (M = Zr, Th, U) binary systems and LiF–ZrF_4–ThF_4, LiF–ZrF_4–UF_4 ternary systems using a "splat roller quenching" method. In fact such a superquenching method is a very suitable technique to extend the glass-forming region in the existence diagrams and to isolate glasses which would be unstable if prepared by conventional methods (*31–35*).

Experimental

The starting materials are the oxides ZrO_2 and ThO_2 and the fluorides LiF (Merck) and UF_4 supplied by Cogema; the fluorides ZrF_4 and ThF_4 are obtained from the ZrO_2 or ThO_2 oxides using a 40% HF solution at 100°C and then anhydrous HF gas for 4 hr at 500°C. The mixtures of the fluoride components, well homogenized, are pressed into pellets and heated up to melting in a nickel crucible under argon atmosphere. The glass preparation has been carried out from the melt by "splat roller quenching." The quenching speed can attain 10^6 $ksec^{-1}$. The quenching temperature varies between 800 and 1100°C, depending on the composition of samples. The amorphous state of the materials obtained is checked by X-ray diffraction and optical microscopy.

A DTA study has been carried out with a MDTA 85 Setaram equipment; the samples are in a platinum crucible under nitrogen atmosphere, the heating rate is 5.8°C mn^{-1}.

A hydrolysis study of the obtained glasses has been undertaken: the glass powder is soaked in a fixed volume of water for a given time and the Li^+ ion concentration is measured as a function of time by using an atomic absorption spectrophotometer (Perkin-Elmer 306).

Ionic conductivity measurements have been carried out on vitreous samples by the complex impedance method using a Solartron 1170 frequency response analyzer. The samples are pellets on which gold electrodes are deposited by vacuum evaporation. The frequency range used is 10^{-2}–10^4 Hz and measurements have been carried out between 20 and 160°C for several temperature cycles in argon atmosphere.

Results

Glass Domains

In accordance with the eutectic regions observed in the phase diagrams (*36–38*), following compositions of glasses have been obtained in the binary LiF–MF_4 (M = Zr, Th, U) systems:

$Li_xZr_{1-x}F_{4-3x}$ $(0.50 \leq x \leq 0.60)$

$Li_xTh_{1-x}F_{4-3x}$ $(0.46 \leq x \leq 0.80)$

$Li_xU_{1-x}F_{4-3x}$ $(0.50 \leq x \leq 0.85)$

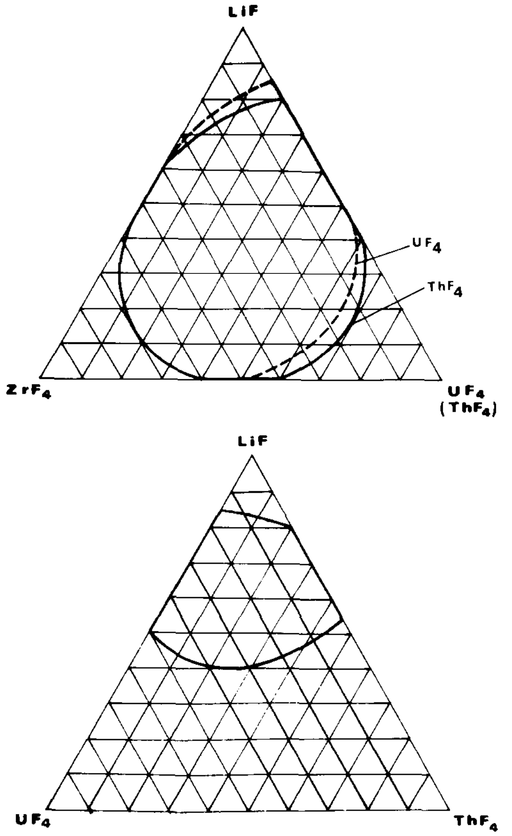

FIG. 1. Vitreous domains in the $LiF–ZrF_4–ThF_4$, $LiF–ZrF_4–UF_4$, and $LiF–ThF_4–UF_4$ ternary diagrams.

The vitreous domain is clearly larger for Th or U than for Zr. This result can be explained by the smaller size of Zr in glasses where the tetravalent cations are obviously the network formers.

Glasses corresponding to concentrations of LiF greatly exceeding 60 mole% have been isolated with ThF_4 and UF_4. A comparison of these materials with glasses belonging to the quaternary $LiF–ZrF_4–BaF_2–ThF_4$ (*29*) and $LiF–ZrF_4–BaF_2–LaF_3$ (*39*) systems shows that glasses may have a high lithium content when the other cations present are highly charged.

Three large vitreous domains have been detected in the ternary $LiF–ZrF_4–ThF_4$, $LiF–ZrF_4–UF_4$, and $LiF–ThF_4–UF_4$ systems. They are shown in Fig. 1.

Hydrolysis

The obtained glasses are stable at open air. However, at room-temperature UF_4-based glasses are quickly hydrolyzed in presence of water, leading to a mixture of crystallized phases. In similar conditions ThF_4-based glasses are more stable. After 24 hr no crystallization can be detected by X-ray diffraction. However, slow dissolution of the glasses has been shown by atomic spectrophotometry (Fig. 2).

Thermal Properties

The results obtained by DTA measurements are shown as an example in Fig. 3 for $Li_{0.60}U_{0.40}F_{2.20}$: transition temperature T_G, crystallization temperature T_C, and melting temperature T_M are successively observed. The thermal properties of some glasses are collected in Table I. We have introduced the thermal data of the glasses belonging to the $LiF–ZrF_4–BaF_2–ThF_4$ system for comparison.

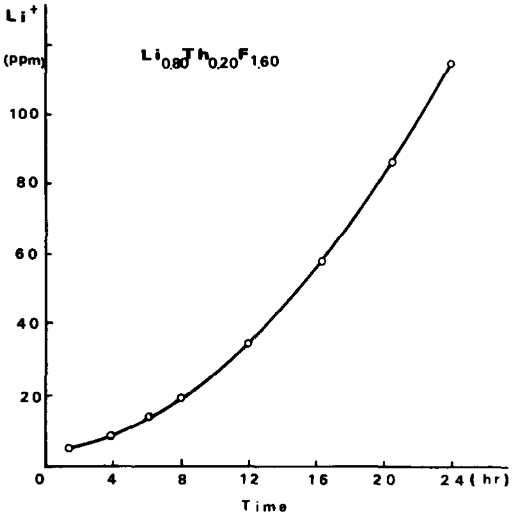

FIG. 2. Variation of Li^+ concentration with soaking time in presence of water for $Li_{0.80}Th_{0.20}F_{1.60}$.

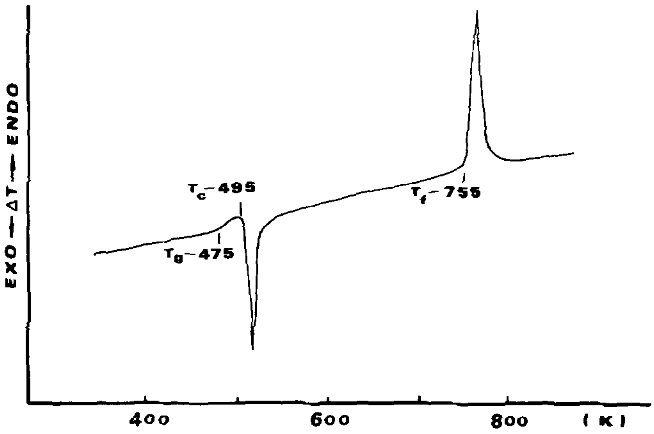

FIG. 3. DTA pattern of $Li_{0.60}U_{0.40}F_{2.20}$.

The Li dependence of the stability ratio $(T_C - T_G)/T_G$ is given in Fig. 4 for fluoride glasses prepared either by "splat roller quenching" (set 1) or obtained by classical methods (set 2). It can be noticed that the stability of both series of materials decreases when the Li^+ concentration increases. An analogous result had been obtained for glasses with composition $(CuI)_x(CuPO_3)_{1-x}$ (*40*). On the other hand the stability indices of set 1 materials are clearly weaker than those belonging to set 2, a result which is consistent with the fact that the former ones can only be prepared by a superquenching technique and hence are less stable.

TABLE I

THERMAL PROPERTIES OF SOME INVESTIGATED GLASSES

Composition	T_G (K)	T_C (K)	$T_C - T_G$ (K)	$\frac{T_C - T_G}{T_G}$
$Li_{0.60}Th_{0.40}F_{2.20}$	504	518	14	0.028
$Li_{0.65}Th_{0.35}F_{2.05}$	507	529	22	0.043
$Li_{0.70}Th_{0.30}F_{1.90}$	514	529	15	0.029
$Li_{0.80}Th_{0.20}F_{1.60}$	485	496	11	0.023
$Li_{0.50}U_{0.50}F_{2.50}$	452	485	33	0.073
$Li_{0.60}U_{0.40}F_{2.20}$	479	495	16	0.033
$Li_{0.70}U_{0.30}F_{1.90}$	469	490	21	0.045
$Li_{0.80}U_{0.20}F_{1.60}$	473	499	26	0.055
$Li_{0.20}Zr_{0.20}Th_{0.60}F_{3.40}$	649	705	56	0.086
$Li_{0.20}Zr_{0.40}Th_{0.40}F_{3.40}$	595	628	33	0.055
$Li_{0.60}Zr_{0.20}Th_{0.20}F_{2.20}$	445	457	12	0.027
$Li_{0.80}Zr_{0.10}Th_{0.10}F_{1.60}$	433	445	12	0.028
$Li_{0.20}Zr_{0.25}U_{0.55}F_{3.40}$	524	561	37	0.071
$Li_{0.20}Zr_{0.40}U_{0.40}F_{3.40}$	504	542	38	0.075
$Li_{0.20}Zr_{0.55}U_{0.25}F_{3.40}$	475	515	40	0.084
$Li_{0.40}Zr_{0.30}U_{0.30}F_{2.80}$	485	512	27	0.056
$Zr_{0.575}Ba_{0.3375}Th_{0.0875}F_{3.325}$	593	673	80	0.135
$Li_{0.20}Zr_{0.60}Ba_{0.15}Th_{0.05}F_{3.10}$	535	621	86	0.161
$Li_{0.20}Zr_{0.50}Ba_{0.20}Th_{0.10}F_{3}$	528	621	93	0.176
$Li_{0.25}Zr_{0.40}Ba_{0.25}Th_{0.10}F_{2.75}$	525	638	113	0.215
$Li_{0.45}Zr_{0.30}Ba_{0.15}Th_{0.10}F_{2.35}$	505	570	65	0.129
$Li_{0.60}Zr_{0.20}Ba_{0.10}Th_{0.10}F_{2}$	493	536	43	0.087
$Li_{0.60}Zr_{0.10}Ba_{0.10}Th_{0.20}F_{2}$	515	569	54	0.105
$Li_{0.60}Ba_{0.10}Th_{0.30}F_{2}$	553	613	60	0.108

Structural Aspects

A large number of publications on ZrF_4- and ThF_4-based glasses belonging to ternary systems such as ZrF_4–BaF_2–LnF_3 and ThF_4–BaF_2–LnF_3 (*41–44*) describe these fluoride glasses as a result of random insertion of cations in a homogeneous and aperiodic anionic packing, the cations having approximately the same coordination as in the crystallized fluoride glasses (*45*).

As a consequence, the ZrF_4- and ThF_4-based glasses would be formed by a three-dimensional array of various polyhedra around network former cations, i.e., ZrF_n ($n = 6, 7, 8$) ThF_n ($n = 8, 9$), and LnF_8, the network periodicity being broken by modi-

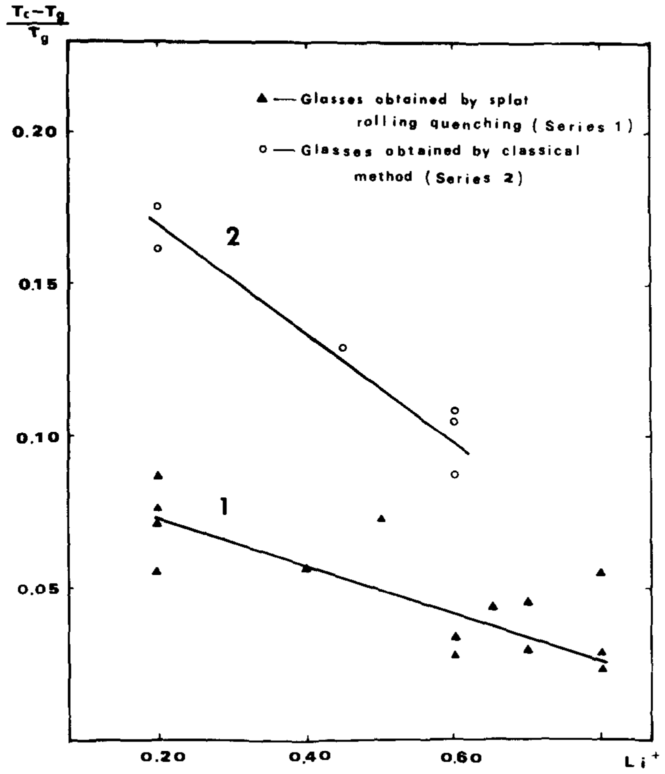

FIG. 4. The Li-dependence of the stability ratio $(T_C - T_G)/T_G$ for fluoride glasses.

fier cations such as Ba^{2+} *(46)*. EXAFS and optical studies have shown that Th^{4+} and U^{4+} cations are 8- and even partially 9-coordinated *(47–49)*.

These structural features have been noticed for glasses containing no or only small amounts of alkaline fluorides. The extrapolation to glasses involving only mono- and tetravalent cations is not obvious: a structural investigation, for instance by Raman laser spectroscopy, has to be carried out prior to definitive conclusion.

Ionic Conductivity

Binary systems LiF–MF₄ (M = *Zr*, *Th*, *U*). The variation of conductivity vs reciprocal temperature is given in Fig. 5 for the glasses investigated in the binary systems LiF–MF_4 (M = Zr, Th, U). For the three series $Li_xM_{1-x}F_{4-3x}$, σ can be expressed in the considered temperature range, by a Arrhenius-type relation: $\sigma = \sigma_0 \exp(-\Delta E_\sigma/kT)$, where σ_0 is constant and ΔE_σ the activation energy related to the diffusive motion of the carriers.

The three series have the same preexponential term σ_0 within uncertainty limits ($\log \sigma_0 = 3.0 \pm 0.4$). This value of $\log \sigma_0$ is very close to that observed previously for glasses belonging to the quaternary LiF–ZrF_4–BaF_2–ThF_4 system ($\log \sigma_0 = 2.8 \pm 0.4$). Hence, it seems to be independent of the glass preparation technics. The quasi-constancy of the term σ_0 implies that the conductivity increases of all these materials result mainly from a decrease in ΔE_σ.

Figure 6 gives the variations of $\log \sigma$ at 60

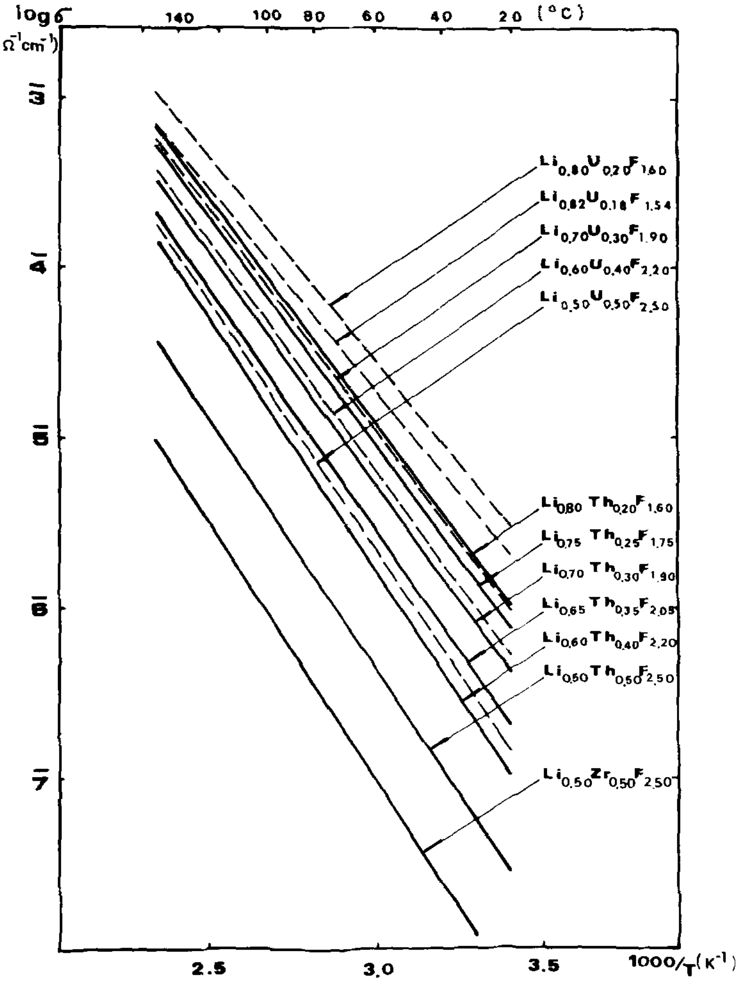

FIG. 5. Variation of log σ vs reciprocal temperature for some glasses obtained in the LiF–MF_4 (M = Zr, Th, U) systems.

and 120°C and the activation energy ΔE_σ as a function of lithium concentration.

A comparison of the electrical properties of glasses with similar lithium concentrations shows that the performance of the $Li_xM_{1-x}F_{4-3x}$ materials improve from M = Zr to M = Th and then to M = U (*50*). For instance, at a given temperature

$$\sigma_{Li_{0.50}Zr_{0.50}F_{2.50}} < \sigma_{Li_{0.50}Th_{0.50}F_{2.50}} < \sigma_{Li_{0.50}U_{0.50}F_{2.50}}.$$

Whatever the transport properties within the $Li_xTh_{1-x}F_{4-3x}$ and $Li_xU_{1-x}F_{4-3x}$ systems seem essentially connected with the Li^+ concentration. As x increases the conductivity and activation energy are, respectively, increasing and decreasing functions of the Li concentration. The better conductivities are obtained for the compositions close to the upper limits of the vitreous domain. Such a phenomenon can be accounted for either by increasing Li^+–Li^+

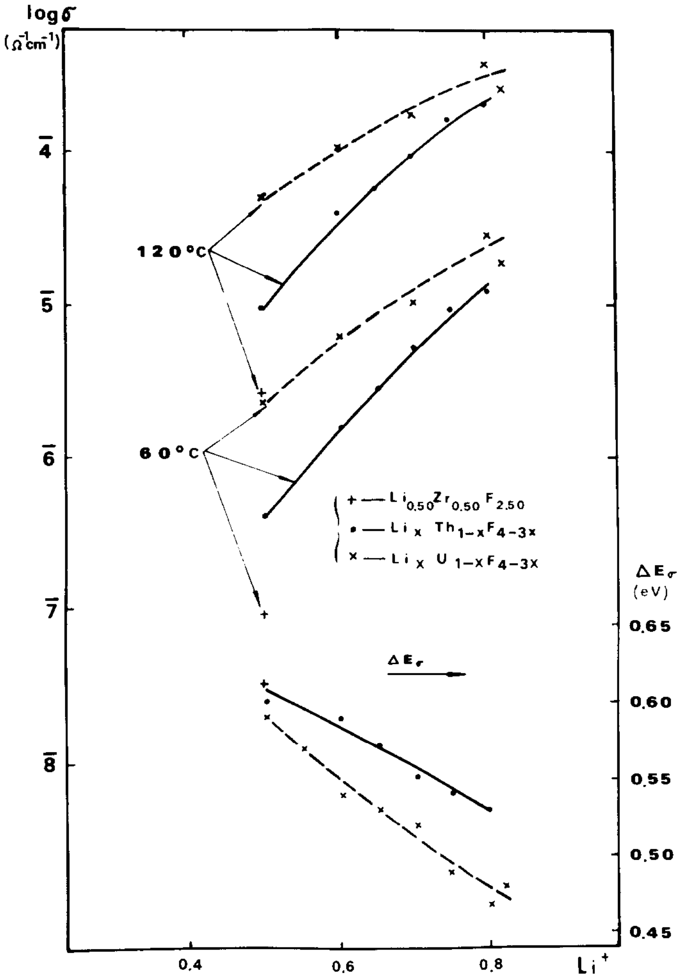

FIG. 6. Variation of log $\sigma_{60°C}$, log $\sigma_{120°C}$ and ΔE_σ as a function of Li concentration.

repulsions or by stronger competition between the Li–MF_n bonds which makes the Li^+ ions more mobile.

Figures 7a and b give the Li^+ concentration dependence of $\sigma_{120°C}$ and ΔE_σ for the glasses belonging to the LiF–MF_4 (M = Zr, Th, U) and LiF–ZrF_4–BaF_2–ThF_4 systems. The representative points of $Li_xM_{1-x}F_{4-3x}$ are located in the lengthening of the curves relative to quaternary glasses. The ^{7}Li NMR study of quaternary glasses (*30*) has shown that for $x > 0.20$ the transport properties depend only on the Li^+ concentration. It results from Fig. 7 that such a conclusion can be extended to $Li_xM_{1-x}F_{4-3x}$ glasses with higher Li^+ concentrations ($0.50 \lesssim x \lesssim 0.85$). For clarity the fluoride glasses belonging to the various binary, ternary, and quaternary systems studied here will be formulated in the following $Li_xZr_\alpha Ba_\beta Th_\gamma F_{4-3x-2\beta}$ (with $\alpha + \beta + \gamma = 1 - x$).

Figure 7b gives the composition dependence of ΔE_σ for some nonfluoride glasses $(LiCl)_x(B_2O_3 - yLi_2O)_{1-x}$ (y = 0.30 and 0.40) (*51*), $(LiI)_x$–$(LiPO_3)_{1-x}$ (*52*), $(CuI)_x$–$(CuPO_3)_{1-x}$ (*40*), and $(AgI)_x$–$(AgPO_3)_{1-x}$

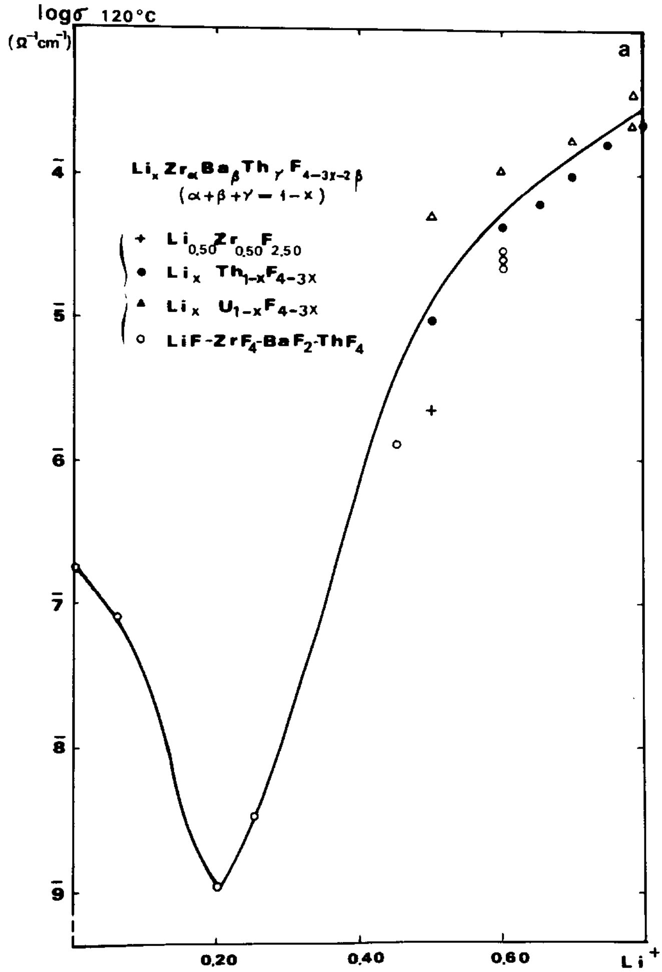

FIG. 7(a). The Li$^+$ dependence of log $\sigma_{120°C}$ for some glasses of the LiF–MF_4 (M = Zr, Th, U) and LiF–ZrF_4–BaF_2–ThF_4 systems.

(*10*). The structure of those materials consists of a covalent boron–oxygen or phosphor–oxygen network in which the halogen ions are diluted without showing noticeable interactions with the glassy lattice (*53, 54*). Figure 7b shows for all those materials a similar behavior of ΔE_σ with increasing x: a quasi-linear portion of the graph and a final tendency to flatten out at different minimum values which seem to depend on the solubility of the halide ions in the oxide matrix. The variation of ΔE_σ with x for the $Li_xZr_\alpha Ba_\beta Th_\gamma F_{4-3x-2\beta}$ fluoride glasses exhibits the same shape for $x > 0.20$. A study of the fluorides glasses by Raman spectroscopy will allow us to determine the existence or not of a structural analogy.

Ternary systems. Large vitreous domains have been detected within the LiF–ZrF_4–ThF_4, LiF–ZrF_4–UF_4 and LiF–ThF_4–UF_4 ternary systems (Fig. 1). The various glasses obtained follow an Arrhenius-type

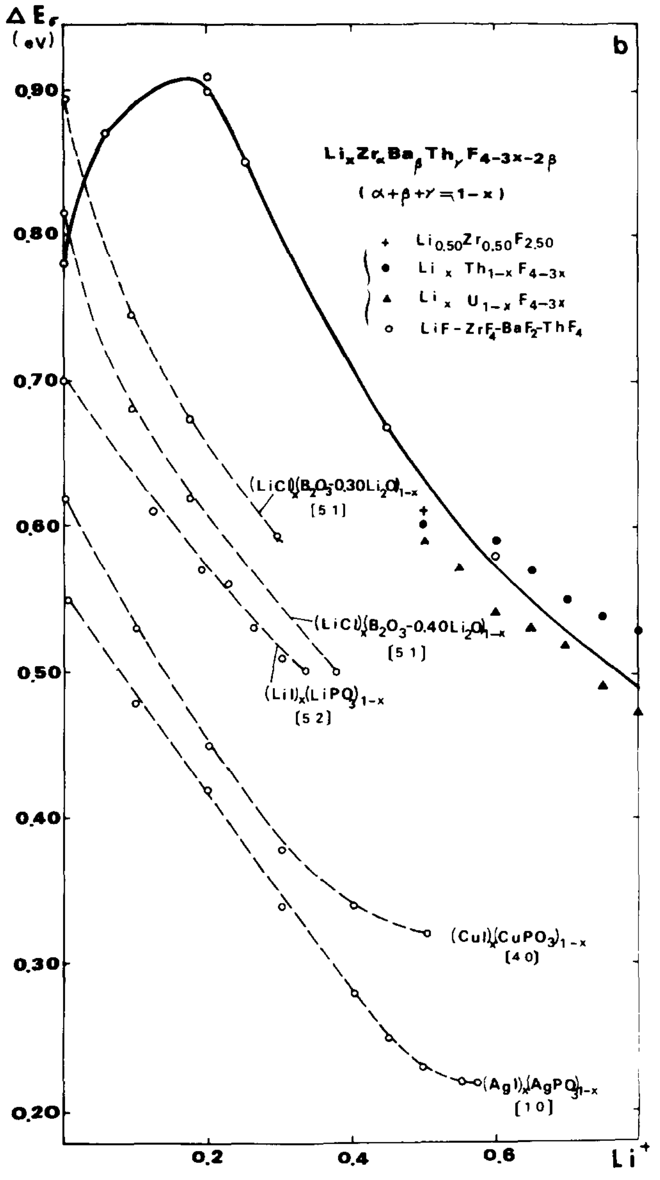

FIG. 7(b). Variation of ΔE_σ as a function of x for some series of glasses, $\mathrm{Li}_x\mathrm{Zr}_\alpha\mathrm{Ba}_\beta\mathrm{Th}_\gamma\mathrm{F}_{4-3x-2\beta}$ $(\alpha + \beta + \gamma = 1 - x)$, $(\mathrm{LiCl})_x(\mathrm{B_2O_3\text{-}yLi_2O})_{1-x}$ $(y = 0.30$ and $0.40)$, $(\mathrm{LiI})_x(\mathrm{LiPO_3})_{1-x}$, $(\mathrm{CuI})_x(\mathrm{CuPO_3})_{1-x}$, and $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$.

conductivity law similar to that of the glasses belonging to the LiF–$M\mathrm{F}_4$ (M = Zr, Th, U) binary systems.

To account for the composition dependence of the transport properties inside ternary domains, we have plotted as significant examples in Fig. 8 the variation of log $\sigma_{60^\circ\mathrm{C}}$ vs $M_1/(M_1 + \mathrm{Zr})$ (M_1 = Th, U) ratio for some series of $\mathrm{Li}_{0.50}(M_1,\mathrm{Zr})_{0.50}\mathrm{F}_{2.50}$ and $\mathrm{Li}_{0.80}(M_1,\mathrm{Zr})_{0.20}\mathrm{F}_{1.60}$ glasses.

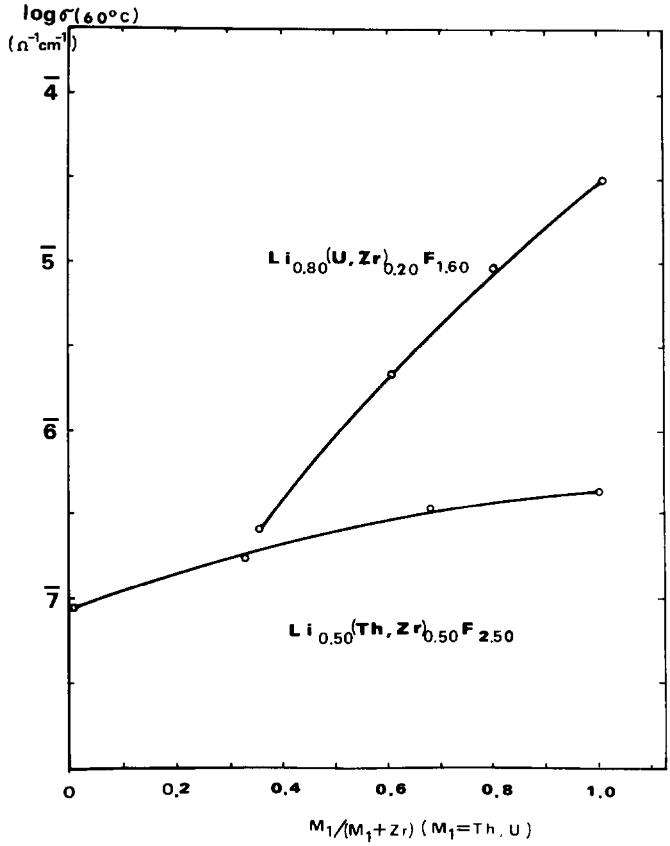

FIG. 8. Variation of log $\sigma_{60°C}$ as a function of $M_1/(M_1 + \text{Zr})$ ratio (M_1 = Th, U) for some series of glasses of $\text{Li}_{0.50}(M_1,\text{Zr})_{0.50}\text{F}_{2.50}$ and $\text{Li}_{0.80}(M_1,\text{Zr})_{0.20}\text{F}_{1.60}$ compositions.

Conclusions similar to those proposed for the binary glasses can be drawn for the ternary glasses: (1) the transport properties improve when the Li^+ concentration increases; (2) substitution of M_1 to Zr in $\text{Li}_x(M_1\text{Zr})_{1-x}\text{F}_{4-3x}$ (where M_1 = Th, U) leads to better performances. The latter effect is enhanced as the Li^+ concentration increases.

Conclusions

The "splat roller quenching" technique has allowed us to isolate within the LiF–$M\text{F}_4$ (M = Zr, Th, U) systems, new fluoride glasses containing very high LiF concentrations (up to 85% mole). Investigation of electrical properties has shown the performance improvement with increasing Li^+ concentration. The transport properties locate those materials inside a large family of fluoride glasses, the formula of which can be written $\text{Li}_x\text{Zr}_\alpha\text{Ba}_\beta\text{Th}_\gamma\text{F}_{4-3x-2\beta}$ ($\alpha + \beta + \gamma = 1 - x$).

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