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D. Ravaine, W. Perera, M. Minier. ALKALI FLUORIDE CONTAINING ZrF_4 - BASED GLASSES : ELECTRICAL PROPERTIES AND NMR INVESTIGATION. Journal de Physique Colloques, 1982, 43 (C9), pp.C9-407-C9-410. 10.1051/jphyscol:1982978 . jpa-00222507

HAL Id: jpa-00222507

<https://hal.science/jpa-00222507>

Submitted on 1 Jan 1982

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ALKALI FLUORIDE CONTAINING ZrF_4 -BASED GLASSES : ELECTRICAL PROPERTIES AND NMR INVESTIGATIOND. Ravaine, W.G. Perera and M. Minier⁺*Laboratoire d'Energétique Electrochimique, B.P. 44, 38401 Saint Martin d'Hères, France*⁺*Laboratoire de Spectrométrie Physique, B.P. 53, 38041 Grenoble, France*

Résumé.— Des résultats récents, obtenus sur des verres à base de ZrF_4 contenant des fluorures alcalins, sont utilisés pour l'interprétation des mécanismes de conduction anionique dans les verres fluorés. Des mouvements locaux d'ions fluorure apparaissent au voisinage des cations modificateurs de réseau ; les déplacements longue distance sont, quant à eux, reliés à l'arrangement des polyèdres formateurs de réseau.

Abstract.— New results obtained on alkali containing ZrF_4 -based glasses from electrical and NMR measurements are used for the interpretation of the anionic conduction mechanism in fluoride glasses. Local F^- motions arise in the vicinity of modifier cations while long range displacements are related to the network former polyhedron arrangement.

In the past five years, fluoride glasses have been discovered in various chemical systems (1-3). Among them, ZrF_4 -based glasses exhibit the highest conductivities due to fluoride ions, available in the amorphous state (4). However, their use as solide electrolytes is still submitted to further improvement of the ionic conductivity and to a better knowledge of the anionic conduction mechanism.

This paper deals with the transport properties of ZrF_4 -based glasses and presents new results obtained from electrical and NMR measurements in alkali fluoride containing glasses.

1. **Structural considerations.**— The glass forming tendency of ZrF_4 has been shown to result from the existence of different ZrF_n ($n = 6, 7$ and 8) polyhedra presenting a large variety of F-M-F bond angles and many possibilities in the local arrangement (5). The vitreous network is built up from the association of these polyhedra sharing corners or edges ; unlike crystalline fluorozirconates, the periodicity of the lattice is broken by the large Ba^+ cations which act as network modifiers. Computer simulated vitreous structure (6) leads to expect that, on the average, 3 (over 7) fluorines are unshared. The role of ThF_4 and of the rare earth fluorides is less obvious. Unlike ZrF_4 , they cannot give vitreous phases when only associated to network modifiers. In practice, they are necessary in order to obtain stable glasses. The size and crystallochemistry of these cations lead to consider that they are incorporated in the vitreous network. The stabilization mechanism could result from the existence of polyhedra differing in their size from ZrF_n polyhedra. The vitreous network is then built up from greater variety of polyhedraⁿ giving more possibilities in the local arrangement. For this reason, they are defined as network stabilizers.

Alkali fluorides can be incorporated in large amounts in a ternary glass. It has been shown that the alkali ions act as network modifiers (7) with octahedral coordination except for Li^+ ion which, at low concentrations, is tetrahedrally surrounded and plays the role of a network former (8). It is therefore of interest to determine if these different structural behaviours have any influence on the anionic transport properties.

2. **Experimental methods.**— The electrical conductivity is measured by the complex impedance plot technique. Disk shape samples*, 13 mm in diameter and 1 mm thick,

* The samples have been prepared in the laboratory of Chimie Minérale D, Rennes

have been coated by platinum sputtering and annealed at 50°C below their glass transition temperature, T_g , for one day. The electrical impedances are measured with an impedancemeter (Alcatel) or; for high impedance modulus, with a capacitance bridge (General Radio) at frequencies ranging from 5Hz to 500kHz.

In order to determine the contribution of alkali ions to the conductivity, a cell involving the investigated glass sample between two Li^+ reversible electrodes (Li_xMoO_2) has been used. Any reliable results from the Tubandt's method would require unreasonably long term measurements. We here compare the stationary current to the initial current after application of a d.c. voltage. This leads to underestimate the anionic conductivity and only gives an upper limit for the Li^+ conductivity.

Pulsed NMR experiments have been performed with a home made pulsed spectrometer on ^{19}F and ^7Li nuclei.

3. Experimental results. - Plots of the electrical complex impedances measured at a given temperature exhibit the well known circular arcs with the center below the real axis. It has been shown that these curves represent the electrical properties of the bulk sample. The ohmic resistance of the sample and its conductivity are deduced from the intersection of the circular arc with the real axis. For all the studied glass samples, the conductivity follows an Arrhenius law :

$$\sigma = \sigma_0 \exp (-E_\sigma/RT)$$

where E_σ is the activation energy for conduction and σ_0 a pre-exponential factor independent of the temperature T . This is illustrated on figure 1 for different alkali containing ZrF_4 -based glasses.

Fig. 1- Conductivity Arrhenius plot for different glass compositions.

On table I are given : the investigated glass compositions (a free alkali glass is also included for comparison), the glass transition temperatures, the values of σ at 200°C and the activation energy for conduction E_σ .

The measurement of the cationic transport number has been performed at 80°C on a Libath glass sample. The upper limit for t_{Li^+} has been found equal to 20 %. As the electronic conductivity is likely negligible, one concludes that the fluorine transport number exceeds 80 %.

TABLE I

NAME	COMPOSITION (m %)	T _g (°C)	σ_{200}^{200} (10 ⁻⁶ Ω ⁻¹ cm ⁻¹)	E _σ (eV)
Bath 8	58.7ZrF ₄ - 31.3BaF ₂ - 10ThF ₄	320	7.10	0.76
Nabath	50ZrF ₄ - 20BaF ₂ - 22.5NaF - 7.5ThF ₄	270	1.15	0.87
Rbbath	57.5ZrF ₄ - 28.7BaF ₂ - 5RbF - 8.8ThF ₄	290	2.30	0.88
Libath	50ZrF ₄ - 22BaF ₂ - 20LiF - 8ThF ₄	250	0.65	0.90
Libalth	57ZrF ₄ - 30BaF ₂ - 6LiF - 2AlF ₃ - 5ThF ₄	275	9.4	0.87
Libalath	49ZrF ₄ - 16BaF ₂ - 22LiF - 5LaF ₃ - 8ThF ₄	250	1.35	0.91
Linaly	40ZrF ₄ - 27LiF - 25NaF - 5YF ₃ - 3AlF ₃	200	3.9	0.91
Linalth	40ZrF ₄ - 25LiF - 27NaF - 4AlF ₃ - 4ThF ₄	200	6.4	0.95

The spin-spin relaxation times measured for both ¹²F and ⁷Li nuclei between 120 and 267°C on the Libath glass sample, show similar activated behaviours with an activation energy of .14 eV (Fig. 2).

Around the glass transition temperature, a new mechanism occurs which may be related to the large change of viscosity in this temperature range.

Fig. 2 - Inverse of ¹⁹F and ⁷Li spin-spin relaxation times in a log scale vs. inverse of temperature.

4. Discussion. - Table I shows that the BaF₂-MF substitution results in increasing the resistivity and the activation energy for conduction. Thus, it seems unlikely that the alkali ions participate to the conduction. The activated process observed on the ⁷Li spin-spin relaxation time T₂ is then certainly due to the modulation of dipole-dipole interactions between F⁻ and Li nuclei. The decrease in conductivity could result of the M⁺ ions fixing the mobile F⁻ ions. On the other hand, small concentrations of substitutional LiF (Libalth) leads to a slight increase of the conductivity which confirms the different structural behaviours of the Lithium.

It appears that the addition of network former polyhedra of different size than ZrF_n favours the fluorine displacement.

NMR investigations performed on alkali free ZrF_4 -based glasses have clearly shown the existence of local motions of fluorine, characterized by an activation energy of 0.2 eV (9). These motions are specific of the glass structure as is shown by the disappearance of the corresponding narrow line in a recrystallized sample. It is then appropriate to assume that the local motions take place in the vicinity of the network modifier cations. This idea finds some support from the change in activation energy observed on T_2 (0.2 $\rightarrow$ 0.14 eV) when substituting the barium ions for lithium ions as modifiers. Finally, long range displacements characteristic of conduction processes appear not to be related to local motions: the activation energies are very different and vary in a different manner with the $BaF_2 \rightleftharpoons LiF$ substitution (0.8 $\rightarrow$ 0.9 eV ; 0.2 $\rightarrow$ 0.14 eV). These ideas are consistent with the weak variations of conductivity (long range motions) with the concentration of network modifiers in a given glass system (4).

The conductivity is then mostly related to the network former polyhedra arrangement. The previous observations lead to assume that the existence of polyhedra of various shape and size is an important factor since it is a source of non-bridging fluorines. When moving, these fluorines involve an exchange of coordinations between two neighbouring former polyhedra. Among all the investigated fluoride vitreous phases, the best conductivities have been observed in the ZrF_4 -based glasses. This provides a confirmation of the above hypothesis since Zirconium is known for its ability to change its coordination.

The situation is then very different from the oxide glasses where the conductivity is strongly dependant of the network modifier concentrations.

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