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ALKALI FLUORIDE CONTAINING ZrF₄ -BASED GLASSES : ELECTRICAL PROPERTIES AND NMR INVESTIGATION

D. 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

Abstract.- New results obtained on alkali containing ZrF₄-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.

1. Structural considerations.— The glass forming tendency of ZrF₄ has been shown to result from the existence of different ZrF₄⁻ (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 ThF₄ and of the rare earth fluorides is less obvious. Unlike ZrF₄, 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 ZrF₄ polyhedra. The vitreous network is then built up from greater variety of polyhedra 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 Minerale D, Rennes
have been coated by platinum sputtering and annealed at 50°C below their glass transition temperature, Tg, 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 50kHz.

In order to determine the contribution of alkali ions to the conductivity, a cell involving the investigated glass sample between two Li⁺ reversible electrodes (Li₂MnO₃) 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 19F 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:

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

where E_a is the activation energy for conduction and $\sigma_0$ a pre-exponential factor independent of the temperature T. This is illustrated on figure 1 for different alkali containing ZrF₄-based glasses.

![Fig. 1](image-url) 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 $\sigma$ at 200°C and the activation energy for conduction E_a.

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

<table>
<thead>
<tr>
<th>NAME</th>
<th>COMPOSITION (m %)</th>
<th>Tg(°C)</th>
<th>$\sigma_{200}$ (10^-6~-1cm^-1)</th>
<th>$E_\sigma$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath 8</td>
<td>58.7ZrF$_4$ - 31.3BaF$_2$ - 10ThF$_4$</td>
<td>320</td>
<td>7.10</td>
<td>0.76</td>
</tr>
<tr>
<td>Nabath</td>
<td>50ZrF$_4$ - 20BaF$_2$ - 22.5NaF - 7.5ThF$_4$</td>
<td>270</td>
<td>1.15</td>
<td>0.87</td>
</tr>
<tr>
<td>Rbbath</td>
<td>57.5ZrF$_4$ - 28.7BaF$_2$ - 5RbF - 8.8ThF$_4$</td>
<td>290</td>
<td>2.30</td>
<td>0.88</td>
</tr>
<tr>
<td>Libath</td>
<td>50ZrF$_4$ - 22BaF$_2$ - 20LiF - 8ThF$_4$</td>
<td>250</td>
<td>0.65</td>
<td>0.90</td>
</tr>
<tr>
<td>Libalth</td>
<td>57ZrF$_4$ - 30BaF$_2$ - 6LiF - 2AlF$_3$ - 5ThF$_4$</td>
<td>275</td>
<td>9.4</td>
<td>0.87</td>
</tr>
<tr>
<td>Libalath</td>
<td>49ZrF$_4$ - 16BaF$_2$ - 22LiF - 5LaF$_3$ - 8ThF$_4$</td>
<td>250</td>
<td>1.35</td>
<td>0.91</td>
</tr>
<tr>
<td>Linaly</td>
<td>40ZrF$_4$ - 27LiF - 25NaF - 5YF$_3$ - 3AlF$_3$</td>
<td>200</td>
<td>3.9</td>
<td>0.91</td>
</tr>
<tr>
<td>Linalth</td>
<td>40ZrF$_4$ - 25LiF - 27NaF - 4AlF$_3$ - 4ThF$_4$</td>
<td>200</td>
<td>6.4</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The spin-spin relaxation times measured for both $^{12}$F and $^7$Li nuclei between 120 and 267°C on the Libath glass sample, show similar activated behaviours with an activation energy of 1.4 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 $^{19}$F and $^7$Li spin-spin relaxation times in a log scale vs. inverse of temperature.](image)

4. Discussion. - Table I shows that the BaF$_2$-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 $^7$Li spin-spin relaxation time $T_2$ 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 substitutonal 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 ZrF₄ favours the fluorine displacement.

NMR investigations performed on alkali-free ZrF₄-based glasses have clearly shown the existence of local motions of fluorine, characterised 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 Tₑ (0.2 ± 0.14 eV) when substituting the baryum 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 BaF₂ → LiF substitution (0.8 ± 0.9 eV; 0.2 ± 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 ZrF₄-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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