Electrical conductivity of glasses and glass-ceramics in the Li$_2$O-CdO-Al$_2$O$_3$-SiO$_2$ system

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ABSTRACT.—Electrical conductivity of glasses and glass-ceramics in the Li$_2$O-CdO-Al$_2$O$_3$-SiO$_2$.

Electrical conductivity measurements at ambient temperature on 10Li$_2$O·(20-40) CdO·(70-50)SiO$_2$ (wt%) glasses have been carried out after several controlled nucleation and crystallization thermal treatments. The conductivities on original glasses are in the -7.50×10$^{-10}$ - 10$^{-6}$ Ω$^{-1}$ cm$^{-1}$ range, while the values for the wide family of different glass-ceramics obtained from thermal treatments are in the 1.2-4.06×10$^{-13}$ Ω$^{-1}$ cm$^{-1}$ interval. The relation between conductivity and crystalline phases composition (mainly, lithium disilicate and lithium metasilicate) is finally discussed.

RESUMEN.—Conductividad eléctrica y materiales vitrocerámicos de Li$_2$O-CdO-Al$_2$O$_3$-SiO$_2$.

Se han realizado medidas a temperatura ambiente de la conductividad eléctrica de vidrios de composición: 10Li$_2$O·(20-40) CdO·(70-50)SiO$_2$ (% en peso) después de ser sometidos a diversos tratamientos térmicos de nucleación y cristalización controlada. La conductividad de los vidrios originales alcanza valores entre -7,50 y 10,60×10$^{-10}$ Ω$^{-1}$ cm$^{-1}$, mientras que para la amplia gama de materiales vitrocerámicos obtenidos por tratamientos térmicos varía entre 1,2 y 4,06×10$^{-13}$ Ω$^{-1}$ cm$^{-1}$. Se discute en este trabajo la relación entre los diversos valores de conductividad con el contenido y composición de las fases cristalinas que se forman en estos materiales que son fundamentalmente disilicato y metasilicato de litio.

1. INTRODUCTION

The crystallisation behavior of original glasses and glass-ceramics from the Li$_2$O-CdO-SiO$_2$ system, such as density, thermal expansion, microhardness, and flexure rupture modulus, has been described previously (1, 2).

Both effects of Cd$^{2+}$ ions as very polarizable cations (3) and Li$^+$ as very movable cations can give interesting electrical properties to these materials. Otherwise, Li$_2$O in glasses and Li$_2$O·2SiO$_2$ or Li$_2$O·SiO$_2$ crystalline phases in glass-ceramics are promising compounds as nuclear fuel for fusion reactors. The simultaneous presence of a neutron absorber such as CdO (σ = 2354 b) can be very interesting considering this nuclear application. Therefore, electrical properties have been determined. The effect of the thermal neutron irradiation on physical and technological properties have been described in previous papers (4, 5).
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2. MATERIALS AND METHODS

Glasses and glass-ceramics were obtained by electric melting of Li₂CO₃, CdO, and SiO₂ mixtures at 1300°C for 2 h in Al₂O₃-SiO₂ crucibles. The formulated compositions (in weight percent) were: A-2, 10Li₂O·30CdO·60SiO₂; A-3, 10Li₂O·40CdO·50SiO₂; and A-5, 10Li₂O·60CdO·30SiO₂. The chemical analysis of the resulting glasses has been reported (2). Glass-ceramic materials were obtained by thermal treatments between 550°C and 700°C for 2 h.

The electrical properties here determined have been: Dielectric permittivity at ambient temperature on plane circular samples, 15 mm in diameter and 3 mm thick. These measurements were performed in the 80-50000 kHz range with a Q-meter 260-Ap. The electrical resistivity has been carried out in a voltmeter-ammeter and a nanoammeter operating in c.c., at 23.5 volt and 120°C. This test temperature was used due to the large results dispersion obtained at ambient temperature. The relative humidity and different microstructures of this type of glass-ceramics (1) can give rise to water absorption and, consequently, to anomalous results at ambient temperatures.

Prismatic samples, 15 by 10 by 3 mm with gold evaporated onto larger faces, were used.

3. RESULTS AND DISCUSSION

The Figure 1 shows the results obtained for the electrical conductivity of the glasses and glass-ceramics considered in the present work. For the original glasses the conductivity values (Ω cm⁻¹) are: \( \sigma(A-2)=7.5\times10^{-13} \), \( \sigma(A-3)=10.6\times10^{-13} \), and \( \sigma(A-5)=8.8\times10^{-13} \).

These electrical conductivity data indicate that this property increases their values when the SiO₂/Li₂O ratio decreases. Therefore, the Li⁺ is strongly bonded in the glassy [SiO₄]⁻ tetrahedra due to its high field intensity.

As is well known, the high polarizability of the Cd²⁺ ions produces a distortion of the glassy structure, promoting an increase in the electrical conductivity when the percentage of this element increases in the glass composition (3). However, the Al₂O₃ added to the glass composition from the crucible used in melting stabilizes the glass network, decreasing the electrical conductivity.

With respect to the effect of thermal treatment during 2 hours on the original glasses, contradictory results are obtained. There is an increase in conductivity when the original glasses are subjected to a heat treatment at 550°C for 2 h. Thus, it seems that the structural ordering prior to crystallization (or phase separation glass-in glass immiscibility) phenomena (Fig. 2) promotes the electrical conduction in the material. It is necessary to point out that at this temperature crystallization is not still detected by XRD (1). Similarly, at closer temperatures such as 600°C for 2 h (Fig. 3) it can be observed phase separation droplets and precrystallization domains like in A-3 glass. If the continuous glassy matrix increases in Li⁺ and Cd²⁺ content, as has been proven by EDX micro-analysis the conductivity increases in the same way.

![Fig. 1. — Electrical conductivity variation on the A-2 glass versus the thermal treatment (for 2 hours) and the crystalline phase content.](image1)

![Fig. 2. — Electrical conductivity variation on the A-3 glass versus the thermal treatment (for 2 hours) and the crystalline phase content.](image2)
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Fig. 3.—Microstructure observed by TEM-replica on glasses: a) A-2; b) A-3 and c) A-5 heat treated at 600°C for 2 hours.

For the thermal treatments at higher temperatures (650°C) the conductivity at A-2 and A-3 compositions decreases due to bulk crystallization, because of the locking of Li⁺ and Cd²⁺ in crystal-

line silicate phases (Fig. 4). However, in glass-ceramics of A-5 composition the behaviour is quite different. Thus, the electrical conductivity of the glass-ceramic produced by heating the A-5 glass at 650°C for 2 h (31% crystalline) is $1.44 \times 10^{-12}$ Ω⁻¹ cm⁻¹, a value far greater than that of the original glass. In this case CdO · SiO₂ is the main crystalline phase and possibly the polarizability of the Cd²⁺ in the silicate structure is greater than for Li⁺ in the lithium metasilicate (Fig. 5).

Fig. 4.—Microstructure observed by SEM on glass-ceramics obtained from the a) A-2 and b) A-5 glasses heat treated at 650°C for 2 hours.

A-5 COMPOSITION

![Graph showing electrical conductivity variation on the A-5 glass versus the thermal treatment (for 2 hours) and the crystalline phase content.]

The electrical conductivity for materials obtained by thermally treating compositions A-2 and A-3 at 700°C shows a small increase due to two effects: a decrease in the amount of the crystalline phase and the existence of liquid-liquid phase separation in the residual glass (1). In the glass-ceramics produced from the A-5 composition heat treated at 700°C, the electrical conductivity shows a large increase. In this case, the proportion of crystalline lithium metasilicate increases, so a higher relative Li⁺ mobility in this metastable phase could increase the conductivity simultaneously with the higher Cd²⁺ content of the residual glassy phase.

G-c obtained during longer thermal treatment times (28 hours at 600°C) depict a very low conductivity for A-2 composition and lower than for A-3. This is due to the high content of crystalline phases (23%) for the A-2 g-C, while the A-3 glass-ceramic only show a smooth turbidity due to a very small crystallization or glass phase-separation. The A-5 g-C obtained at 600°C for 28 hours is constituted by similar content of crystallization volume fraction that the A-2 g-C. However, its Li₂O · SiO₂ phase content is higher giving rise to an increase in electrical conductivity.

Fig. 5.—Electrical conductivity variation on the A-5 glass versus the thermal treatment (for 2 hours) and the crystalline phase content.
Estudio de la conductividad iónica de Li⁺ en compuestos con estructura tipo NZP

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RESUMEN.—Estudio de la conductividad iónica de Li⁺ en compuestos con estructura tipo NZP.

La preparación de muestras de Li₂Zr₂(PO₄)₃ por vía cerámica y vía gel conduce a dos fases diferentes ambas con estructura tipo NZP para parámetros reticulares distintos. La conductividad iónica que los discos prensados y sinterizados de estas dos fases presentan, en el intervalo entre 25 y 400 °C, revelan mecanismos de conducción diferentes. En la muestra preparada vía gel se produce un cambio en el valor de la energía de activación de 0.17 eV a 0.42 eV a unos 175 °C, mientras que en la preparada vía cerámica es de 0.19 eV en todo el intervalo de temperaturas estudiado. La conductividad iónica a 400 °C es de 3.85×10⁻⁸ (S/cm) para la muestra preparada vía gel y de 2.28×10⁻⁸ (S/cm) para la preparada vía cerámica.

Dos muestras no estequiométricas preparadas vía gel presentan también comportamientos diferentes pero semejantes entre sí. Li₂Zr₂(PO₄)₃(OH) presenta una energía de activación de 0.45 eV y una conductividad de 1.01×10⁻⁴ (S/cm) a 400 °C, hand, glass-ceramics conductivity is lightly lower than commercial pyroflam glass-ceramics.

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REFERENCES


Table I

VALUES RANGES OF ELECTRICAL PROPERTIES OF Li₂O-CdO-Al₂O₃-SiO₂ GLASSES AND GLASS-CERAMICS AND CONVENTIONAL SIMILAR GLASSY MATERIALS

<table>
<thead>
<tr>
<th>Glasses</th>
<th>Commercial Pyroflam</th>
<th>Li₂O-CdO-Al₂O₃-SiO₂ (Opal and opaques)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (Ω·cm⁻¹)</td>
<td>9.7</td>
<td>≈ 12</td>
</tr>
<tr>
<td>Permittivity (K)</td>
<td>7</td>
<td>7.8-9.0</td>
</tr>
<tr>
<td>Dielectric losses</td>
<td>6</td>
<td>5.0-70.0</td>
</tr>
<tr>
<td>tan δ×10⁵</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Estudio de la conductividad iónica de Li⁺ en compuestos con estructura tipo NZP

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ABSTRACT.—Study of the ionic conductivity of Li⁺ compounds with NZP structure.

The preparation of Li₂Zr₂(PO₄)₃ by a ceramic method and by a gel route leads to two different phases both with NZP structure but different lattice parameters. The ionic conductivity of the pressed and sintered disks for the two phases, in the range of 25-400 °C, reveals different conductivity mechanisms. For the sample prepared by gel-route, a change in the activation energy is observed (from 0.17 eV to 0.42 eV) between 150 and 200 °C but for the sample prepared by ceramic method the activation energy of 0.19 eV in the whole interval studied. The ac conductivity at 400 °C of sintered pellets is 3.85×10⁻⁸ (S/cm) for the sample prepared by gel-route and 2.28×10⁻⁸ (S/cm) for the sample prepared on the ceramic route.

Two non-stoichiometric samples prepared by gel-route show both a new different behaviour. Li₂Zr₂(PO₄)(OH) presents an activation energy of 0.45 eV and an ionic conductivity at 400 °C of 1.01×10⁻⁴ (S/cm); while for Li₂Zr₁.₇₅(PO₄)₃ the activation energy of 0.42 eV and an ionic conductivity at 400 °C of 1.75×10⁻⁴ (S/cm).