

Study of Ionic Conductivity of Lanthanum Oxychloride

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Summary: The ionic conductivity of lanthanum oxychloride has been measured by using the method of plotting graphs of impedance in the plane complex. The ionic conductivity measurements were made for the temperature limits (300 - 1400)^oC. The determined activation energy at low temperature agrees with that measured for PbCl₂ and SrCl₂ as given respectively,^{1,2,3} while the value at high temperature shows a slight agreement with measurements made on ThO₂-YO_{1.5} 15%, La₂O₃-CaO and La₂O₃-SrO of Hammou⁴ and Vanbaelinghem⁵

Introduction

The present work is concerned with the study of ionic conductivity of lanthanum oxychloride as a good new electrolyte with respect to the chloride ions. This selection of LaOCl as an electrolyte is based on its lattice structure figure (1), which is tetragonal in the form of layers, forming flattened prisms similar to that of PbFCl^{1,6}. The unit cell of the lattice structure of LaOCl is shown in figure (2) with Lattice parameters as $a=4,119 \text{ \AA}$, $b=6,888 \text{ \AA}$. C. Tubandt and M. Schmidt have studied the conductivity of PbFBr (which is identical in structure to LaOCl) and found that its conductivity is purely anionic with $t_{\text{F}^-} = 1 - t_{\text{Br}^-} = 0.87$.

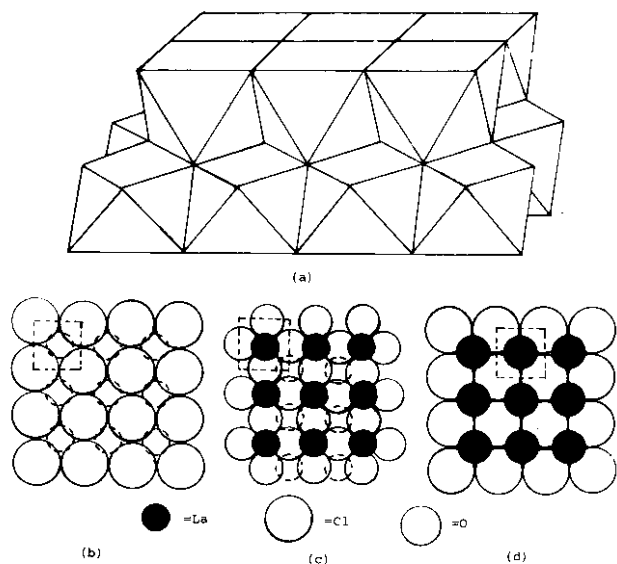


Fig (1) The Lattice Structure of Lanthanum Oxychloride.

Experimental

Preparation of LaOCl

The lanthanum oxychloride compound has been prepared at the Inorganic Applied Chemistry Laboratory, Montpellier, France; the method involved passing a current of oxygen at a rate of $20 \text{ cm}^3 \cdot \text{S}^{-1}$ over

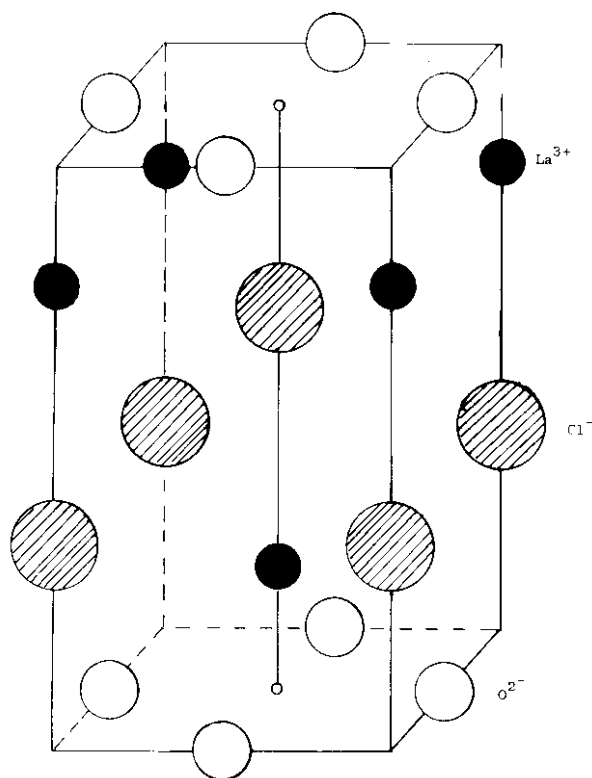


Fig (2) Crystal Structure of Lanthanum Oxychloride.

dry and pure LaCl_3 (99,99%) contained in a platinum crucible and heated to 400°C in an electrical furnace. From the resulting powder compound, blocks of the following dimensions were prepared, $l=0.75$ mm, $S=0.53$ mm and $d=0.43$ mm. The metallic electrodes used for the conductivity cells were made of platinum from commercial paints.

Conductivity measurements

The measurements of conductivity were made following the procedures of various workers 8, thru 12, which involves plotting the graphs of impedance of symmetrical cell of the type metal/electrolyte/ metal, in a plane complex. Impedance measurements were made in frequency range 5Hz to 500 KHz with an Alcatel (type 2531) impedancemeter, which measure the impedance model ranged between 1Ω and $1\text{M} \Omega$ with an angle ϕ , the argument of impedance.

Results and Discussion

The results of the impedance measurements for symmetrical cell Pt/LaOCl/Pt are shown in figure (3). The diagrams presented in the figure indicate two parts that are characterised by two frequency regions. Firstly, the high frequency region in which the measured impedance represents an arc featuring the electrolyte conduction. The arc centres lie on a straight line, which determine, the $\frac{\alpha}{2}$ angle with the real axis. This angle is characteristic of the material and can be attributed to a scattering of the local conductivity. Secondly the low frequency region is indicated by the beginning

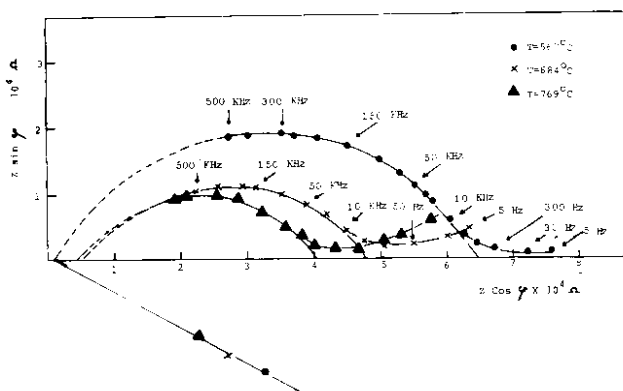


Fig (3) Complex Impedance diagrams for the symmetrical cell pt/ LaOCl / pt.

of another arc that can be completed on increasing the temperature. This is due to the polarization of the electrodes.

Variation of the conductivity of lanthanum oxychloride has been obtained as a function of temperature in the range $300 < T < 1400^\circ\text{C}$, and is shown in the figure (4). It is of interest to note that this result is a preliminary one for this new electrolyte. According to figure (4) two regions can be recognized, the first is a region with $300 < T < 1000^\circ\text{C}$ is a region with $300 < T < 1000^\circ\text{C}$ having an activation energy of $E_{a1} = 0.49$ ev. While the second region at temperature region $100 < T < 1400^\circ\text{C}$ with an activation energy of $E_{a11} = 0.89$ ev.

Comparison of the lower value of activation energy with that of PbCl_2 and SrCl_2 studied by SCHOONMAN¹ and O'Keefe² respectively shows a good agreement in the measured value. This can be explained in terms of the migration of chloride ions caused by the mechanism of vacancy migration.

On the other hand, the second results at high temperature leads us to propose primarily the following suggestions.

- Participation of oxide ions of extrinsic origin in the transportation of current where the defects in the oxygen sublattice are due to the presence of impurities of type CaO and BaO in the crystal of LaOCl. This procedure is in agreement with results obtained by Hammou⁴ and F. Vanbaelinghem⁵ for other compounds listed in table (I) conducting by oxygen.

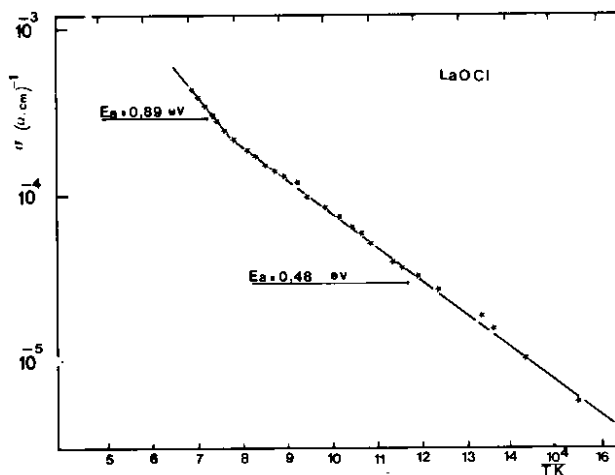


Fig (4) Ionic Conductivity of Lanthanum Oxychloride electrolyte as a function of temperature.

Table (I) Values of Activation energy after Hammou⁴
 and F Vanbaelinghem⁵

Compound	Ea(eV)
ZrO ₂ -YO _{1.5} 15%	0.7 (4)
ThO ₂ -YO _{1.5} 15%	0.92 (4)
La ₂ O ₃ -CaO	0.9 (5)
La ₂ O ₃ -SrO	0.7 (5)

- b. Formation of anti-frenkel pair in chloride sublattice of this structure which is represented by the equation $\text{Cl}_{\text{Cl}} \times \longrightarrow \text{Cl}_{\text{I}}' + \text{V}_{\text{Cl}}^{\bullet}$ where the conduction is affirmed by the vacancy mechanism, in this case the energy of formation of this pair is too small.

Therefore, the results of the second part may be either due to the increase of chloride site vacancies of extrinsic origin or due to the presence of other species Contributing to the transport such as Cl_I' or oxide ions, and hence the value of energy of activation which is in a good agreement with those in table (I) leads us to suggest that the results of this part could be due to the presence of oxide ions of extrinsic origin contributing to the transport.

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