STUDY OF THE IONIC CONDUCTIVITY OF SOME FLUORIDES OF MONOVALENT AND TETRAVALENT ELEMENTS

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Recently some interest has attached to ionic conductivity in the fluorides of metals with large cation radius because of the high fluorine mobility in these materials.

A.c. conductivity measurements using the complex impedance method were carried out on sintered samples and showed that some binary fluorides of monovalent elements (M^{I} = K, Rb, Tl) and tetravalent elements (M^{IV} = Zr,Hf, Th, U) exhibit an appreciable ionic conductivity at moderate temperature :

σ at 200°C (Ω^{-1} cm^{-1})	
Tl_3ZrF_7	3.5×10^{-3}
Tl_2ZrF_6	1.1×10^{-2}
$Tl\ ZrF_5$	5×10^{-4}

A single crystal study of Tl_3ZrF_7 shows that this compound crystallizes in the cubic system with space group Fm3m and cell parameter a = 9.34 Å. Therefore its crystal structure may be related to that of $(NH_4)_3ZrF_7$ [1 to 3] which is characterized by the presence of $(ZrF_7)^{3-}$ ions with a pentagonal bipyramid as probable configuration. There are two crystallographically independent fluorine ions in position (96 j) of the space group Fm3m with a percentage of occupancy of 20.8 and 8.3 respectively. Thus Tl_3ZrF_7 is an example of fluoride where a three dimensional ionic conductivity occurs due to an incomplete occupation of a special symmetry position and where temperature increase might create rotation of $(ZrF_7)^{3-}$ polyhedra giving rise to an important anionic disorder.

In order to determine the origin of the ionic conductivity in $TlZrF_5$ we have undertaken the determination of the crystal structure of this fluoride from X-ray intensity measurements made with the aid of an automatic four circle diffractometer.

$TlZrF_5$ cristallizes in the monoclinic system with unit-cell dimensions a = 8.112(1) Å, b = 7.927(3) Å, c = 7.929(1) Å, β = 123.99(1)° and space group $P2_1/c$ (N° 14), Z = 4.

In this structure, the Zr^{4+} ion is surrounded by eight F^- ions, the coordination polyhedron being a bicapped trigonal prism. This crystal structure consists of sheets $(ZrF_5)^-$ that may be described as edge-shared and corner-shared bicapped trigonal prisms (ZrF_8). The sheets run parallel to the yOz plane and are bonded together by the Tl^+ ions which are surrounded by twelve F^- ions. This arrangement produces relatively open tunnels in the b direction delimited by the cations. Of the five independent fluorine atoms, two of them, namely F(1) and F(4) are different from the other from the point of view of bonding and are located in these tunnels. Thus they are probably primarily responsible for the high conductivity of this material [4].

With regard to Tl_2ZrF_6, it is the best as far as ionic conductivity is concerned. However its crystal structure is still unknown and its determination is actually under investigation in our laboratory.

All this materials are good electronic insulators and their transport properties due to the high fluorine ion mobilities allow us to think that some of them hold considerable promise for use as solid electrolytes.

1 G.C. HAMPSON and L. PAULING, J. Am. Chem. Soc., 60 (1978) 2702.

2 H.J. HURST and J.C. TAYLOR, Acta Cryst., B.26 (1970) 417.

3 H.J. HURST and J.C. TAYLOR, Acta Cryst., B.26 (1970) 2136.

4 D. AVIGNANT, I. MANSOURI, R. CHEVALIER and J.C. COUSSEINS, to be published.