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IONIC TRANSPORT IN Tl_2ZrF_6 AND RELATED COMPOUNDS

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Due to the large polarizability of the Tl^+ ion, the peculiar role played by this cation as mobile species in fluorides or as cation with a large size associated to the fluorine ion in fluoride ion conductors has been emphasized by several studies carried out in our laboratory on single phases issued from the $TlF-ZrF_4$ system, namely $TlZrF_5$ and Tl_3ZrF_7 .

During the study of the ionic transport properties of various phases of this system, a.c. ionic conductivity measurements performed on sintered polycrystalline samples using the complex impedance method revealed good performances for compositions between 66.6 and 62.5 moles per cent of TlF . The electronic insulator character of these materials was proved by d.c. conductivity measurements using the Van der Pauw's method. In order to specify the ionic transport mechanism the crystal structure of the Tl_2ZrF_6 phase has been determined from single X-ray diffraction data and will be reported. The possibility for this phase to exhibit a non stoichiometric domain will be discussed.

Pulsed NMR techniques has been applied to the study of both ^{19}F and ^{205}Tl nuclei motion. Thermal and frequency dependences of nuclear spin-lattice relaxation times will be reported.

Correlations between structural, electrical and NMR studies will be presented and discussed while comparison with other fluorides of monovalent elements will bring out the role of the thallium.