

## MONOVALENT CATION CONDUCTION IN ZIRCON

U. DAHANAYAKE AND B.S.B. KARUNARATNE\*

*Department of Physics, Faculty of Science, University of Peradeniya, Peradeniya.*

Zircon ( $\text{ZrSiO}_4$ ) is the silicate of Zirconium (the 20<sup>th</sup> most abundant element in the Earth's crust, at 220 ppm), which is one of the oldest terrestrial minerals dated back to 4.2 billion years. Originally associated with igneous deposits, a combination of weathering and natural concentration due to its high density ( $4.7 \text{ g mm}^{-3}$ ) allowed the formation of large secondary deposits in beach sands. It is the most common and widely distributed commercial mineral, and important commercial deposits are mined in Australia, India, Sri Lanka, South Africa and U.S.A.

The crystal symmetry of zircon is tetragonal, with a tetramolecular cell of the dimensions:  $a = b = 6.61 \text{ \AA}$  and  $c = 5.98 \text{ \AA}$ . The prominent structural units are chains of alternating edge-sharing  $\text{SiO}_4$  tetrahedra and  $\text{ZrO}_8$  triangular dodecahedra extending along the  $c$  axis, which are joined laterally by edge-sharing  $\text{ZrO}_8$  dodecahedra. As a consequence of this structural arrangement, octahedral voids ( $\sim 3 \text{ \AA}$ ) that contain no cations are present in the zircon structure. Absence of such cations, in turn, would suggest the feasibility of incorporating foreign cations, such as  $\text{Li}^+$  and  $\text{Na}^+$ , in these fairly large interstitial voids. This paper presents the results of a preliminary study on electrical conductivity behaviour of zircon ceramics consecutively doped with 10 mol%  $\text{Li}_2\text{CO}_3$  and 10 mol%  $\text{Na}_2\text{CO}_3$ . The effect of addition of  $\text{Y}_2\text{O}_3$  on the electrical conductivity of these systems is also discussed.

The conductivity measurements indicated that there was a significant dependence of electrical conductivity of zircon ceramics on temperature and composition. The conductivity of zircon without any dopant was very low, and the value was  $3.83 \times 10^{-6} \text{ S cm}^{-1}$  at  $700 \text{ }^\circ\text{C}$  with the activation energy of 0.76 eV. Zircon doped with 10 mol%  $\text{Li}_2\text{CO}_3$  and 10 mol%  $\text{Na}_2\text{CO}_3$  showed a considerable conductivity enhancement of one order of magnitude with lower activation energies (0.35 eV and 0.29 eV in 10 mol%  $\text{Li}_2\text{CO}_3$  and 10 mol%  $\text{Na}_2\text{CO}_3$ , respectively). The most likely reason why these systems showed a considerable conductivity enhancement would be the increased concentration of interstitial charge carriers in the zircon host structure, resulted upon doping with monovalent cations. This speculation was supported by subsequent X-ray diffraction analysis, which revealed a formation of an interstitial solid solution. Zircon doped with 5 mol%  $\text{Y}_2\text{O}_3$  + 5 mol%  $\text{Li}_2\text{CO}_3$  showed conductivity enhancement of two orders of magnitude, which was the highest in the systems investigated so far. The reason for this large conductivity enhancement might be the improved incorporation of charge compensating interstitial monovalent cations in the zircon structure, resulted upon the substitution of  $\text{Y}^{3+}$  in the place of  $\text{Zr}^{4+}$ . The observed low activation energies would also suggest an interstitial mechanism of electrical conduction in these doped zircon ceramics. Ionic conduction in doped zircon was substantiated by the D.C. polarization tests which revealed that the electronic transference numbers in doped zircon systems were as low as 0.35 whereas it was more than 0.80 in zircon without any dopant.

*Financial assistance by the University of Peradeniya and the Postgraduate Institute of Science is greatly acknowledged.*