ELECTRICAL PROPERTIES OF ZIRCON ($ZrSiO_4$) CERAMICS DOPED WITH DIFFERENT DOPANTS PREPARED VIA SOLID STATE SINTERING ROUTE

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Zircon ($ZrSiO_4$) is an inexpensive natural mineral which is mined in very large quantities throughout the world including Sri Lanka and is recognized as a potential ceramic material for high temperature applications. It has also been proposed as a waste form for nuclear decommissioning and related applications. Although many studies on the properties of zircon requisite for such applications are reported in literature, electrical properties of zircon have received less attention. The results of a study on electrical properties of doped zircon ceramics prepared via solid state sintering route are reported in the present work. In this study, natural zircon powder was used as the starting material whereas Y_2O_3, Yb_2O_3, Eu_2O_3, Fe_2O_3, CaO, MgO, Li_2CO_3 and Na_2CO_3 were used as dopants.

Electrical conductivity of sintered samples was measured using *complex impedance spectroscopy* in the temperature range of 100- 500 °C. The electrical conductivity of zircon without any dopants sintered at 1300 °C for 5 hours was 2.53×10^{-7} S cm^{-1} at 500 °C whereas it was 8.49×10^{-7} S cm^{-1} at 500 °C for zircon without any dopants sintered at 1450 °C for 5 hours. It was observed that Y_2O_3, Fe_2O_3, Li_2CO_3 and Na_2CO_3 doped zircon, with a dopant concentration level of 10 mol %, enhanced the conductivity by one order of magnitude whereas Yb_2O_3, Eu_2O_3, CaO and MgO doped zircon did not show any considerable conductivity enhancement, with the same dopant concentration level. The highest conductivity enhancement which was of two orders of magnitude was observed in doubly doped systems: namely (5 mol % Y_2O_3 + 5 mol % Li_2CO_3) doped zircon and (5 mol % Y_2O_3 + 5 mol % Na_2CO_3) doped zircon. It was also observed that the activation energy values for electrical conduction were quite different from system to system indicating that the rate

controlling conduction mechanism is not identical in these systems. The most probable conduction mechanism in each system has been suggested with the aid of subsequent *Scanning Electron Microscopic (SEM)* analysis. Fe_2O_3 doped zircon showed some interesting magnetic behaviour and hence magnetic measurements were performed using *Vibrating Sample Magnetometry (VSM)* for curiosity. It was revealed that the presence of ferromagnetic Fe_2O_3 grains in the resulting samples has direct implications with the observed magnetic behaviour.

X-ray Fluorescence (XRF) and *Inductively Coupled Plasma (ICP)* analysis of starting zircon powders confirmed the presence of impurities in different concentration levels. Hence, for a comparative study, zircon was synthesized in the laboratory via solid state sintering of precursor oxides (ZrO_2 and SiO_2). The zircon yield in the resulting samples, calculated using *X-ray diffraction (XRD)* data, was dependent on the dopant and the highest zircon yield (100 %) was observed in 10 mol% Fe_2O_3 doped system whereas doping with Li_2CO_3 or Na_2CO_3 completely hindered the zircon formation. Although it was observed that the most of the laboratory synthesized zircon samples resembled their natural zircon counterparts as far as the electrical conductivity values are concerned, the activation energy values were dependent on the synthesis route.

The electrical conductivity of natural zircon single crystals along crystallographic axes *a* and *c* was also investigated. It was observed that the conductivity values measured along *c* axis (σ_c) were constantly higher than those measured along *a* axis (σ_a), which is indicative of the conductivity anisotropy of zircon single crystals. However, it was observed that σ_c/σ_a (for a fixed temperature) varies only from 1.50 to 2.77 in the temperature range of interest.

The flexural strength of some selected zircon particulate composites was determined in 4-point bending mode and it was revealed that the flexural strength of zircon composites were about twofold higher than that of monolithic zircon. The toughening mechanisms in the composites were identified as crack bridging, crack deflection and microcracking by subsequent microstructural analysis performed on the samples.