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ELECTRICAL PROPERTIES OF ZIRCON CERAMICS DOPED WITH DIFFERENT DOPANTS

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ABSTRACT

The electrical properties and dielectric behavior of zircon ceramics with different dopants have been studied as a function of temperature using impedance spectroscopy. The dopants used in this study were Y_2O_3, Fe_2O_3, MgO, Yb_2O_3 and Eu_2O_3. The study revealed that the electrical conductivity and the dielectric constant of doped zircon increased with increasing temperature, irrespective of the dopant. The samples doped 10 mol% Y_2O_3 and 10 mol% Fe_2O_3 showed an enhancement in conductivity. The values were 7.74×10^{-5} S cm^{-1} and 2.01×10^{-5} S cm^{-1} at 700°C respectively. These conductivity values were about one order of magnitude higher than that of zircon without dopants. However, other dopants did not show a significant conductivity enhancement. As such, in this study special emphasis was given to the Y_2O_3 doped zircon system, which showed the highest conductivity. The correlation between the phase distribution of the samples and the conductivity is also discussed.

Keywords: Zircon; Impedance spectroscopy; Electrical conductivity; Dielectric constant

1. INTRODUCTION

Zircon ($ZrSiO_4$) is tetragonal: $I4_1$ / amd, Z=4 and the ideal structure consists of chains of alternating, edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to crystallographic axis c [1]. Zircon is an abundant and inexpensive natural mineral and is mined in very large quantities throughout the world [2] and is recognized as a potential ceramic material for the applications at high temperature due to its good combination of many attractive properties such as low thermal expansion (4×10^{-6} °C^{-1} between 25°C and 1400°C), low thermal conductivity (4 Wm^{-1}°C^{-1}), good chemical stability, excellent thermal shock resistance [3]. Although many studies on structural properties of zircon ceramics have been reported in literature, electrical properties of zircon have received less attention. It was one of the two reasons why this material was selected for this investigation. The other was the superfluity of zircon in the coastal areas of Sri Lanka. This paper presents the results of a preliminary study on electrical properties of zircon ceramics doped with different dopants. It is expected that the presence of defects in the zircon host structure introduced by doping can lead to higher electrical conduction. The effects of dopants, Y_2O_3, Fe_2O_3, MgO, Yb_2O_3 and Eu_2O_3 on electrical properties were investigated.

2. EXPERIMENTAL

In this study zircon sand from the coastal areas of Sri Lanka was used as the starting material. Sri Lanka is world famous for gem quality zircon and it is reported in the literature that Sri Lanka zircon contains low impurities, low OH content and well defined geological age (570 ± 20 million years). The average composition of Sri Lanka zircon is given in Table 1 [4]. The major impurity presents in zircon is HfO_2 and was also confirmed by us using neutron activation analysis.

Although gem quality zircon contains low impurities, zircon sand that was used as the starting

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material in this study, may contain different degrees of impurity levels and would be a significant factor in assessing the electrical properties. In this study the effect of impurities present in the zircon sand on electrical properties was ignored and the undoped zircon samples prepared from sand was used as the base material. As such the effects of intentionally added dopants, Y_2O_3, Fe_2O_3, MgO, Yb_2O_3 and Eu_2O_3 on electrical properties were investigated.

Table 1. Chemical analysis of Sri Lanka zircon [4].

Component	Content (wt %)
SiO_2	33.01
ZrO_2	65.85
HfO_2	0.81
CaO	0.01
Y_2O_3	0.14
ThO_2	0.01
UO_2	0.03
Total	99.86

In this study zircon powders were obtained by crushing zircon sand and by subsequent ball milling with known amounts of dopants. The mixed powders were uniaxially pressed at 200 MPa in a stainless steel die into pellets of 15 mm in diameter and approximately 2 mm in thickness. The green pellets were sintered at 1300°C for 5 hours. The sample was mounted in the sample holder and kept in a horizontal tube furnace. Two platinum plates were used as electrodes and gold paste was used to improve electrical contact between the sample and the electrodes. The impedance data were collected in the temperature range 500°C-700°C during heating and subsequent cooling by using the impedance analyser (4192 LF, HEWLETT PACKARD) in the frequency range 20 Hz-10 MHz. All the conductivity measurements were performed in air. The dielectric constant was also calculated using the complex impedance data. Transference numbers of the Y_2O_3 doped system, which showed the highest conductivity, were determined by using the d.c. polarization method. In this technique, a constant d.c. voltage was applied to the specimen and the current was monitored by a reference resistor and recorded in a chart recorder as a function of time.

The microstructures of the samples were investigated in order to examine whether dopants exist as a second phase or incorporate into the zircon host structure. The SEM (JEOL FX2000) observations were performed by backscattered electron mode, in which the number of backscattered electrons depends on the atomic number of the sample material and the topography of the surface of the sample. In order to eliminate the topographical contrast the surface of the sample was polished to get a smooth finish (1 μm) using SiC abrasive papers and diamond paste. They were then put into an ultrasonic cleaning bath in order to remove any possible impurities collected during the polishing process. Subsequently, it was confirmed that there were no visible scratch marks. The samples were mounted on small metal stands. Then a thin layer of gold was sputtered on the samples to avoid sample charging during SEM observations. In order to investigate the phase distribution in detail, the Energy Dispersive X-ray (EDX) analysis was performed on a JEOL FX2000 microscope, especially for the Y_2O_3 doped system which showed the maximum conductivity enhancement. In the case of EDX analysis, a thin layer of carbon was sputtered on the samples instead of gold prior to the investigations.

3. RESULTS & DISCUSSION

Conductivity and dielectric measurements

The conductivity and dielectric constant of zircon ceramics were found to increase with increasing temperature, irrespective of the dopant. Similar conductivity values were obtained in measurements under heating and cooling at a given temperature, indicating that there were no compositional changes occurred during the measurements. Representative Arrhenius plots of conductivity measured are shown in Fig.1. The conductivity of zircon without a dopant was very low and the value was 3.83×10^{-6} S cm^{-1} at 700 °C, which is comparable with the data reported in the literature [5]. Addition of Y_2O_3 enhanced the conductivity and the sample with 10 mol% Y_2O_3 showed the highest conductivity and the value was 7.74×10^{-5} S cm^{-1} at 700°C. Further addition of Y_2O_3

was not effective to increase conductivity probably by increasing the content of Y_2O_3 as a second phase. Also, Y_2O_3 in concentrations lower than 10 mol%, decreased the conductivity as shown in Fig. 2.

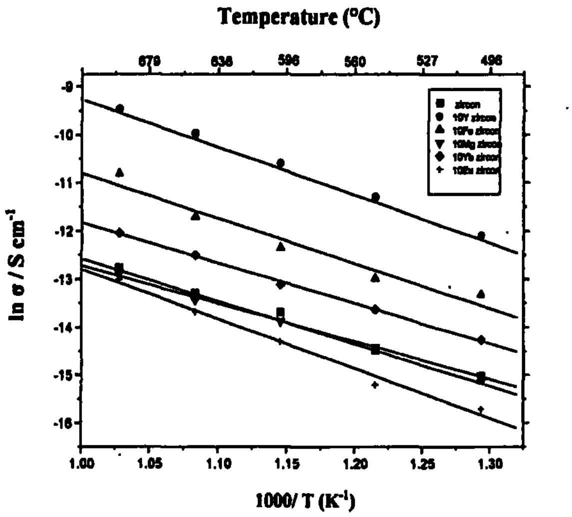


Fig.1 Arrheneus plots of conductivity for zircon without any dopant and 10 mol% Y_2O_3, Fe_2O_3, MgO, Yb_2O_3 & Eu_2O_3 doped zircon

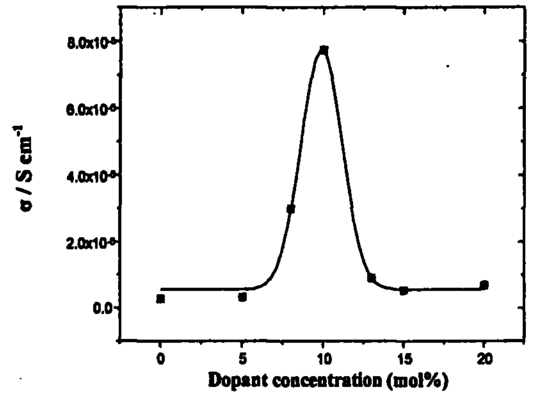


Fig.2 The variation of the electrical conductivity for Y_2O_3 doped zircon with the dopant concentration

Addition of Fe_2O_3 also gave a considerable conductivity enhancement and the sample with 10 mol% Fe_2O_3 showed a value of 2.01×10^{-5} S cm^{-1} at 700°C. The existence of a mixed electronic and ionic conduction in Y_2O_3 doped zircon system, which showed the highest conductivity enhancement, was evident from d.c. polarization tests. The average electronic transference number obtained was 0.45 for 10 mol% Y_2O_3 doped zircon. This was more than 0.75 for the other Y_2O_3 concentrations (Fig. 3). However, Yb_2O_3, MgO and Eu_2O_3 doped zircon did not show any significant conductivity enhancement. It may be due to the fact that these dopants have not been incorporated in the host structure of zircon to give a defect structure. This was evident from subsequent microstructural studies. The most likely reason why Y_2O_3 and Fe_2O_3 doped zircon showed a considerable conductivity enhancement is that Y^{3+} and Fe^{3+} ions could be incorporated in the host structure of zircon [6] creating O^{2-} vacancies to maintain the charge neutrality of the material. These O^{2-} vacancies may take part in the conducting process and would increase the ionic conductivity of Y_2O_3 and Fe_2O_3 doped zircon systems. This phenomenon is analogous to zirconia (ZrO_2) doped with aliovalent cations like Y^{3+} and Ca^{2+} [7]. Yttria Stabilized Zirconia (YSZ) is a well known oxide ionic conductor and is used as the electrolyte of the Solid Oxide Fuel Cell (SOFC).

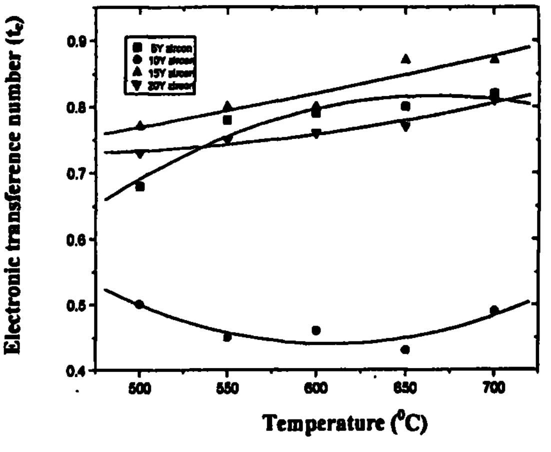


Fig.3 The variation of the electronic transference number (t_e) with temperature for Y_2O_3 doped zircon

It is important to note that the apparent conductivity of a sintered material is also sensitive to its density or porosity of the sample. It is known that the conductivity increases rapidly with densification and gradually approaches that of the bulk material [8]. The density of the samples used in this study was about 80% of the theoretical density of zircon (4.67 g cm^{-3}). Thus, achieving densities close to theoretical density could further enhance the conductivity of these zircon ceramics.

It was also observed that the dielectric constant in 10 mol% Fe_2O_3 doped and 10 mol% Y_2O_3 doped zircon systems, which showed higher conductivity, increased rapidly with increasing temperature. In contrast, the other systems, which showed lower conductivity, showed only a slight increase in the dielectric constant (Fig. 4). Polarization in a material can be due to several types of charge transfer; electronic, molecular, atomic/ionic etc. Electronic polarization is relatively insensitive to temperature and therefore temperature has little effect on the dielectric constant. Polarization due to molecular orientation is opposed by thermal agitation, and the dielectric constant goes down as the temperature increases. Atomic/ionic polarization tends to increase with temperature due to the increase in charge carriers and ion mobility. The increase in dielectric constant with temperature in these systems suggests that atomic/ionic polarization is the dominant polarization mechanism. This may be the reason why the systems having relatively high conductivity showed a rapid increase in dielectric constant with increasing temperature.

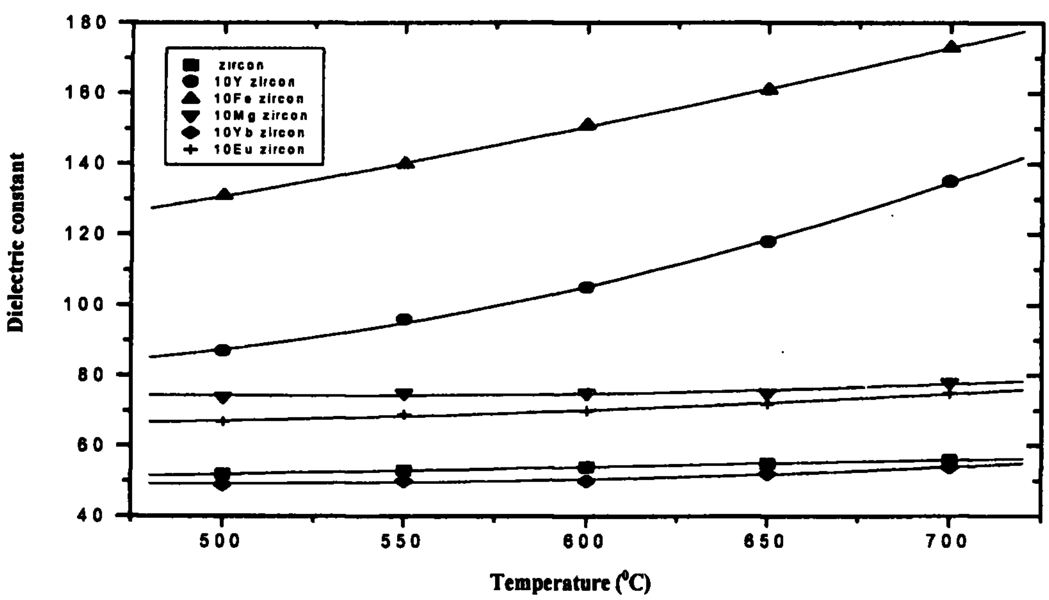


Fig.4 The variation of the dielectric constant for 10 mol% Y_2O_3, Yb_2O_3, Fe_2O_3, MgO and Eu_2O_3 doped zircon with the temperature

Microstructural features of sintered ceramics

The microstructural study indicated that the dopants except Y_2O_3 exist mainly as a second phase having irregular shapes between zircon polycrystals. The typical microstructure of the sintered zircon without dopant is shown in Fig 5. It was observed that the average grain size of zircon polycrystals was in the range 5-6 µm. Significantly high porosity was observed in the microstructures. This is in agreement with the density of the sample obtained using the mass and the geometric dimensions, which was about 80% of the theoretical density. Phase distribution in theY_2O_3 doped zircon was not clearly visible in the backscattered mode because of the poor contrast due to the very close atomic numbers of the constituting elements of zircon; Y=39 and Zr=40. However, the EDX analysis of Y_2O_3 doped zircon indicated that a considerable amount of Y (Fig. 6b) could be found within zircon grains. The EDX study showed that the second phase (clusters of small bright spots in Fig. 6a) contained a significant amount of ZrO_2. This is a special feature in the microstructure of Y_2O_3 doped zircon system and it is worth exploring this effect in a separate study. Yb_2O_3 and Eu_2O_3 both having a higher average atomic number than that of zircon, appeared brighter (Fig.7) where as MgO having a lower average atomic number, appeared darker in the back scattered mode. In both of those cases, no considerable amount of dopants was found within the zircon grains.

4. CONCLUSION

It was observed that conductivity and dielectric constant of zircon ceramic increased, with increasing temperature, irrespective of the dopant. A conductivity enhancement of more than one order of magnitude could be achieved by doping with 10 mol% Y_2O_3 and 10 mol% Fe_2O_3. This enhancement of conductivity is most probably due to the creation of O^{2-} vacancies in the zircon host structure by substitution of Fe^{3+} and Y^{3+} for Zr^{4+}. However, Yb_2O_3, MgO and Eu_2O_3 did not show any considerable conductivity enhancement. This may be attributed to the fact that these dopants have not been incorporated in the host structure of zircon to give a defect structure. As a consequence, doping with these dopants creates no O^{2-} vacancies that are necessary for oxide ionic conduction and hence conductivity is not increased. The density of the sintered samples used in this study was around 80% of the theoretical density. Thus, achieving densities close to theoretical density could further enhance the conductivity of zircon ceramics. The superior high temperature properties and the electrical conduction in zircon based ceramics would make them a potential candidate material for heating elements in high temperature electrical furnaces. The increase in the dielectric constant in these zircon ceramics with temperature suggested that atomic/ionic polarisation is the dominant polarisation mechanism. Hence it is likely that a rapid increase in dielectric constant with temperature could be used as a tool to identify the relatively high ionically conducting systems.

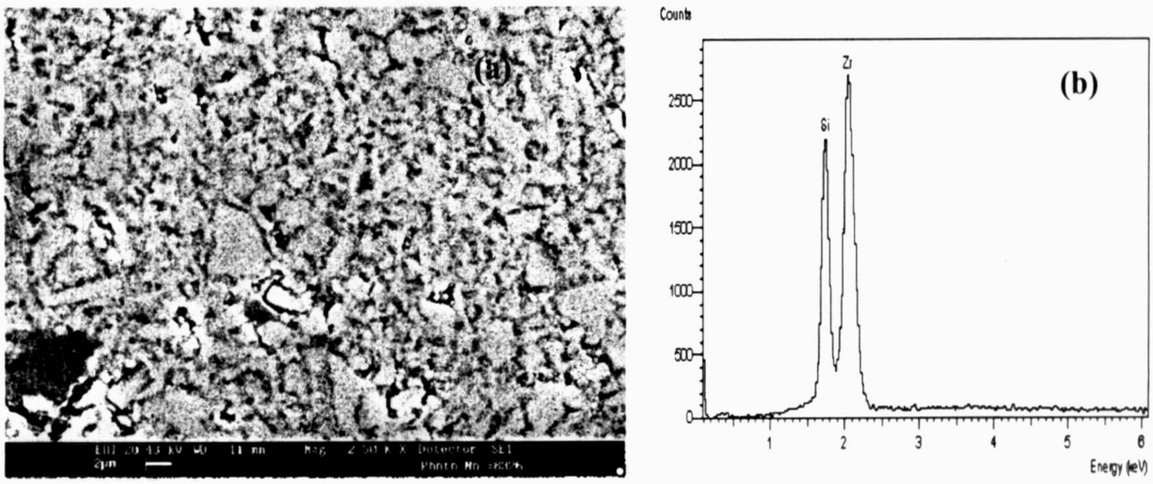
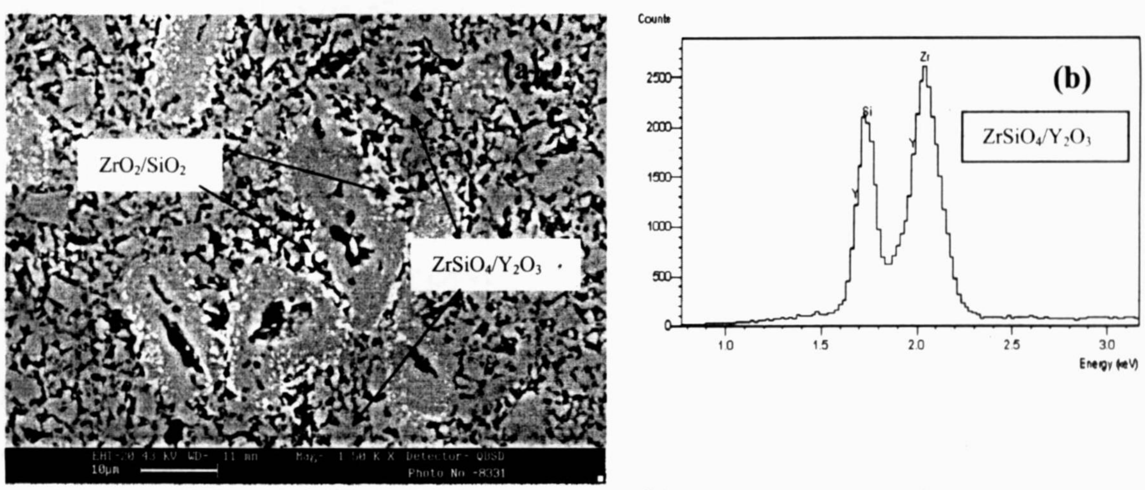


Fig. 5. (a) Secondary scanning electron micrograph of zircon sample prepared from zircon sand, showing the general microstructure. The average grain size is about 5 μm and the porosity is around 20%. (b) EDX spectrum confirming the equimolar composition of $ZrSiO_4$.



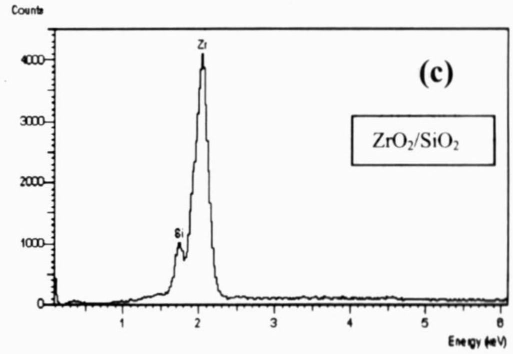
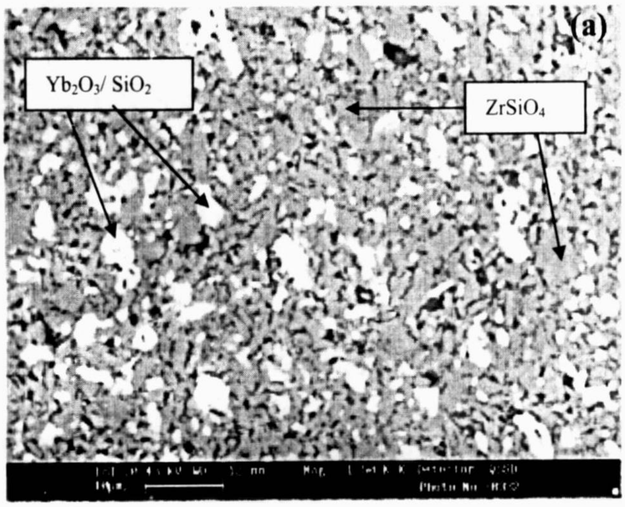
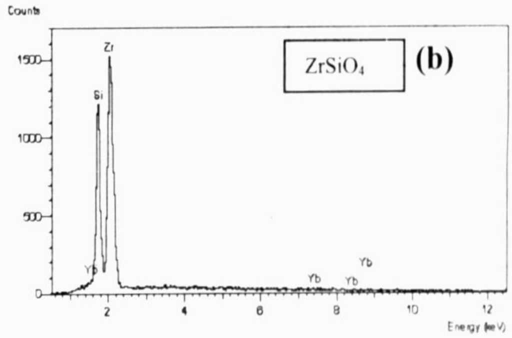


Fig. 6. (a) Backscattered scanning electron micrograph and (b&c) EDX spectra, indicating the phases of $ZrSiO_4/Y_2O_3$ and ZrO_2/SiO_2 in the 10 mol% Y_2O_3 doped zircon sample sintered at 1300°C for 5 hours. (bright areas- mainly ZrO_2/SiO_2; light areas-$ZrSiO_4/Y_2O_3$).





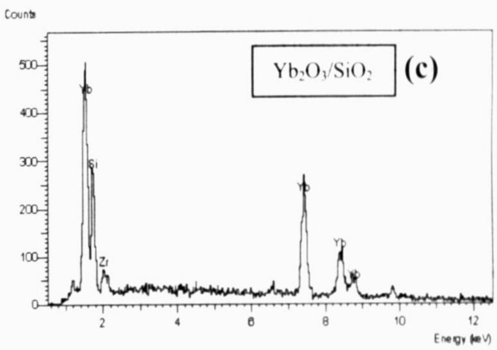


Fig. 7. (a) Backscattered scanning electron micrograph and (b&c) EDX spectra of 10 mol% Yb_2O_3 doped zircon sintered at 1300°C for 5 hours, illustrating the phase distribution. (bright areas- Yb_2O_3/SiO_2; grey areas- $ZrSiO_4$).

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