

EFFECTS OF TEMPERATURE AND IONIZING RADIATION ON SOME PHYSICAL PROPERTIES OF DEVELOPED ZIRCONIA REFRACTORIES

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ABSTRACT

In this manuscript, various samples of alkaline earth, transition element and actinide element oxide-doped zirconia bodies were made by the usual ceramic procedure and firing techniques. Several measurements were undertaken on these materials, comprising X-ray diffraction (XRD), infrared absorption spectra (IR) and direct current (DC) temperature dependence of electrical conductivity before and after an energetic γ -absorbed dose. Results obtained were in conformity with the literature and are explained and discussed on the basis of the interaction of ionizing radiation with doped or stabilized zirconia refractories.

INTRODUCTION

Partially stabilized zirconia finds important applications in industry such as in storage heaters, oxide thermistors, hydrogen generators, oxygen detectors and in high temperature fuel cells. McDevitt and Baum [1] previously utilised the infrared absorption (IR) spectra as a tool for the characterization of different zirconia phases; at the same time they showed that the monoclinic samples with the same X-ray diffraction (XRD) pattern could have considerably different infrared absorption spectra. Dixon et al. [2] suggested that the conductivity increased as the ionic radius of the substituted cation decreased, however, complete evidence of this trend was not presented. On the other hand Strickler and Carlson [3] found that all M_2O_3 - ZrO_2 systems except La_2O_3 formed cubic solid solutions of fluorite type structure, the electrical conductivity of these cubic solid solutions increased as the size of the substituted cation decreased. The interaction of γ quanta with the coulomb nuclear or electron field [4] involves the photoelectric effect, Compton effect and pair production. The present investigation reports the effects of doping and ionizing radiation.

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EXPERIMENTAL

Material synthesis and doping of pure zirconia

The starting materials of pure chemical grade (purity > 99.8%) were ZrO_2 (Prolabo, France), CaCO_3 (BDH), La_2O_3 (BDH) and UO_3 (BDH). Several samples of CaO-, La_2O_3 - and UO_3 -doped zirconia were carefully prepared by the usual ceramic procedure and firing technique. The procedure includes first intimately mixing zirconia with the corresponding molar percentage (up to 6 mol%) of each dopant and grinding in an agate mortar for 1 h. The mixes were then fired in an electric muffle furnace at 1000°C for 3 h. The products were pulverized, ground, compressed into cylindrical pellets (diameter 1.0 cm; thickness 0.2–0.3 cm) at 1000 kg cm^{-2} and sintered at 1150 and 1350°C for 3 h. The doped zirconia bodies produced were then subjected to XRD measurements, and IR-spectroscopy to ensure the propagation of doping and evaluate the phase formed in each case.

X-ray diffraction (XRD) measurements

The CuK_α XRD patterns of the different doped and stabilized zirconia bodies were recorded using a Shimadzu (Japan) X-ray diffractometer Model XD-3. The ground sample was pressed on the standard sample holder. The diffractograms were automatically recorded at a rate of 2° min^{-1} and the chart speed rate was 10 mm min^{-1} at room temperature.

Infrared (IR) absorption spectra measurements

The IR spectra were recorded using the pellet method and the potassium bromide technique. The various samples of doped zirconia, in a concentration ratio of 1 : 50 KBr (Spec. Pure), were ground and vacuum pressed into transparent windows immediately using a suitable die which could be evacuated. The prepared window was then carefully fixed in its holder in the path of the IR beam. The percentage transmittance was automatically recorded against wavenumber (cm^{-1}) using a Pye Unicam SP 1000 infrared spectrophotometer (L.T.D., Cambridge, England) in the range 1400–200 cm^{-1} at room temperature.

DC electrical conductivity measurements

The circuit and mode of measurements used were very similar to those previously described [5] with some modifications. Measurements were made at both room and elevated temperatures up to 550 K and the readings were taken three times 15 min after each temperature equilibration.

^{60}Co γ -radiation exposure

For irradiation studies, the samples were irradiated using a ^{60}Co γ cell at a dose rate of 29 rd s^{-1} . The doped zirconia bodies were exposed to an energetic absorbed γ dose ($3.5 \times 10^7 \text{ rd}$) in air using a ^{60}Co γ cell (300 Ci) at The Arab Institute of Radiation and Isotopes (Dokki, Geiza, Egypt).

RESULTS AND DISCUSSION

The XRD patterns indicate that, with the exception of La_2O_3 -doped zirconia, the doped zirconia bodies comprise both monoclinic and cubic zirconia phases. The ratio of monoclinic to cubic zirconia phases depends highly on sintering temperature, origin of zirconia and molar percentage of dopant (see Fig. 1). This throws light on the thermal stability or pyrolysis of the cubic zirconia solid solutions formed. Alternatively, it was deduced from X-ray data undertaken for uranium-doped zirconia, sintered at 1150 and 1350°C for 3 h, that the cubic doped zirconia (Z-D) undergoes thermal

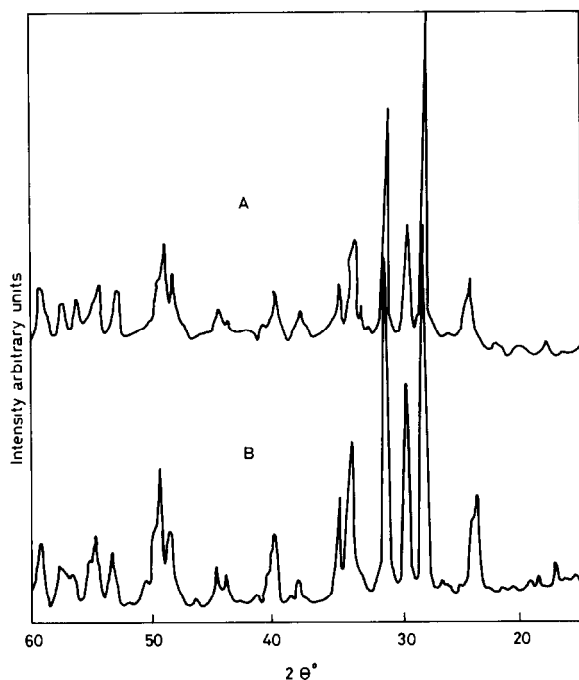
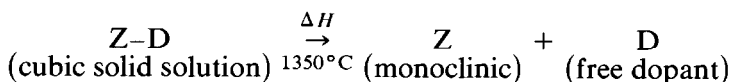
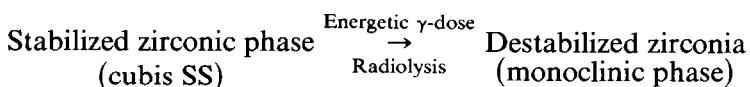


Fig. 1. The $\text{CuK}\alpha$ X-ray diffraction patterns of urania (6 mol%), doped zirconia sintered at 1350°C for 3 h: (B) before and (A) after an absorbed γ -radiation dose ($3.5 \times 10^7 \text{ rd}$).

dissociation partially to monoclinic zirconia (Z) and free dopant (D) as follows:



For the effects of γ radiation, Fig. 1 shows the $\text{CuK}\alpha$ XRD patterns of urania-doped zirconia (6 mol%), sintered at 1350°C before (pattern B) and after (pattern A) an absorbed γ radiation dose (3.5×10^7 rd). It can obviously be seen that, as a result of γ -radiation damage (pattern A), the relative intensity (I/I_0) of the X-ray deflection peak at $2\theta = 30^{\circ}$ (corresponding to the strongest peak of cubic zirconia) decreases, whereas the relative intensity (I/I_0) of the X-ray deflection peak at $2\theta = 28.4^{\circ}$ (corresponding to the strongest peak of the monoclinic zirconia) increases at the expense of the former. This can be explained on the basis that the stabilized zirconia phase undergoes partial γ -radiation-induced destabilization, or γ -radiolysis, which often occurs as a result of γ radiation damage:



This is in agreement with our previous experience of the effects of γ -radiation damage on other stabilized zirconia bodies. However, in the present investigation, the amount of cubic zirconia phase which undergoes destabilization is very small, indicating a high γ -radiation resistance of the stabilized zirconia bodies.

Alternatively, our present data could indicate that once an extensive disorder is introduced by γ radiation (γ -radiation damage) into the doped zirconia crystals, the chemical bonds are considerably weakened. Furthermore, doped zirconia crystals can expand and lose their stabilized structure; i.e., to say doped zirconia bodies undergo destabilization as a result of γ -radiation damage. It can easily be seen that the resistance towards destabilization depends highly on the type and amount of dopant. Abou Sekkina et al. [6] deduced from other materials that the greater the electronegativity difference (ionicity) of the binding, the greater would be the tendency of the crystals to resist extensive structural changes (disordering) by radiation. Thus, in conformity with our previous deduction [6] the relatively high γ -radiation resistance for the present doped zirconia refractories could be attributed to the increased electronegativity difference (ionicity) and hence bond strength as a result of the interaction of ionizing radiation with the dopant ions in zirconia lattices.

For the dependence of IR absorption spectra on the phase constitution of doped zirconia, Fig. 2 shows the infrared absorption spectra of: calcia, pure zirconia, lanthana (4 mol%) and lanthana (6 mol%). From Fig. 2 it can be seen that the IR spectra have one feature in common, namely the lower

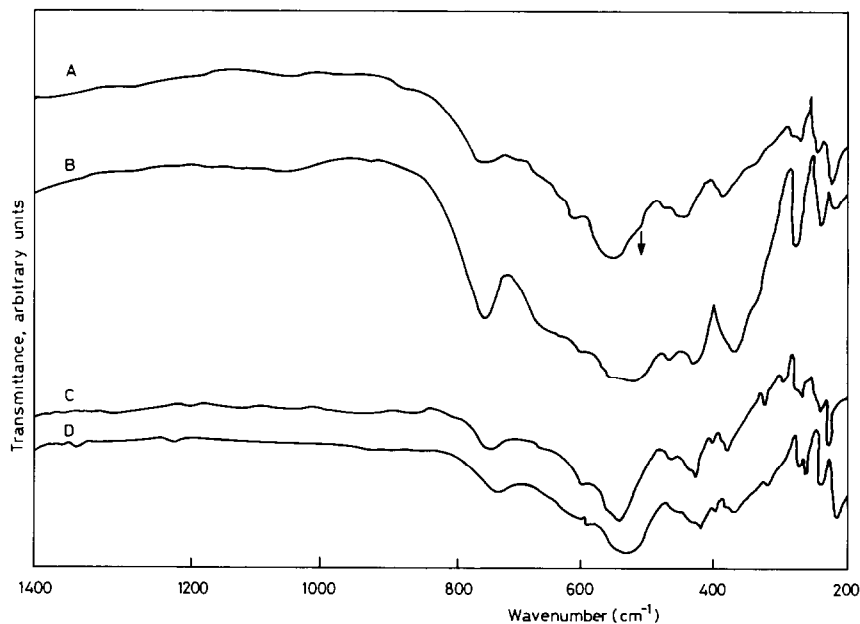


Fig. 2. The infrared absorption spectra of: (A) calcia (6 mol%), stabilized zirconia, 1350 °C for 3 h; (B) pure zirconia (Prolabo, France); (C) lanthana (4 mol%), doped zirconia, 1350 °C for 3 h; (D) lanthana (6 mol%), doped zirconia, 1350 °C for 3 h.

frequency bands are slightly weaker and much broader than the higher frequency ones. As the amount of dopants increases, the absorption bands broaden (see spectra B–D, Fig. 2). This may be attributed to the slight distortion [7,8] of the zirconia lattice from its normal monoclinic crystal form and the decreased degree of crystallinity. This observation is only detected by IR spectra indicating the higher sensitivity of this method to structural changes than XRD. It is also of interest to note that the IR spectrum corresponding to monoclinic zirconia (spectrum B) is slightly sharp and differs in character from that of zirconia containing mixed phases (monoclinic + cubic) as shown in spectrum (A). In accordance with McDevitt and Baum [1], the characteristic IR absorption spectra for the cubic solid solution of zirconia include a very broad band (vb) at 490 cm^{-1} (see Fig. 2, spectrum A).

The results of the XRD and IR studies were in conformity, indicating that doping of zirconia with lanthana produces no fluorite-type structure (cubic solid solution) within the compositional range investigated; this is in accordance with the results of Strickler and Carlson [3]. Thus, in our view, the lanthana dopant remains incorporated in the monoclinic zirconia lattice in the form of periclase or clusters causing lattice imperfections which may lead to a defective crystal lattice; this is reflected in the broadening of bands in the IR spectra and in the X-ray diffractograms. The IR absorption

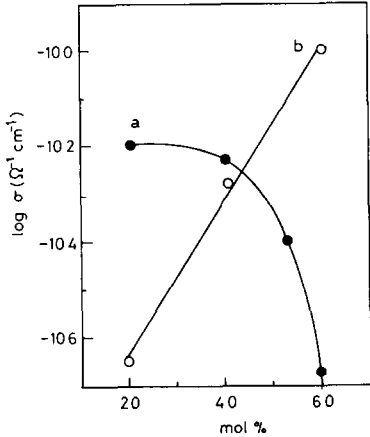


Fig. 3. The variation of DC electrical conductivity at 100°C as a function of mol% of dopant in sintered zirconia refractories (1350°C, 3 h) before (b) and after (a) γ irradiation.

spectra are different for zirconia samples which show the same X-ray diffraction pattern, and it was suggested, therefore, that IR spectra might be more sensitive than X-ray diffraction to small changes in the crystal lattice of zirconia phases. Moreover, it was deduced that the IR spectra vary with the sintering temperature, indicating thermal destabilization of the cubic zirconia phase formed. This implies that the IR spectra may yield practical, new information on the thermal destabilization phenomenon.

It was found that DC electrical conductivity varies exponentially with temperature before (B) and after (A) the energetic γ -dose absorbed (3.5×10^7 rd), according to the well known relation [9]:

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

From this relation, the ΔE values could be calculated and were assumed to correspond to the activation energies of defect mobilities. Thus, Fig. 3 shows the variation of electrical conductivity ($\log \sigma_{100} \text{ ohm}^{-1} \text{ cm}^{-1}$) as a function of dopant (mol%) in sintered zirconia bodies (1350°C, 3 h) before B and after A the absorbed γ dose. Figure 4 shows the variation of activation energy for defect mobilities B, before, and A, after, irradiation, together with the variation of activation energy for carrier liberation, ϕ eV, (C) as a function of mol% of La_2O_3 dopant in the zirconia lattice. The activation energy for carrier liberation could be calculated from Fig. 4 for the materials investigated for the first time using the relation [10]:

$$\phi = \phi_2 - \phi_1$$

where ϕ_2 is the activation energy for conduction after the absorbed γ dose (3.5×10^7 rd), and ϕ_1 is the activation energy for electric conduction before irradiation. Results obtained from conductivity data indicate that the activation energies for conduction before and after irradiation increase with

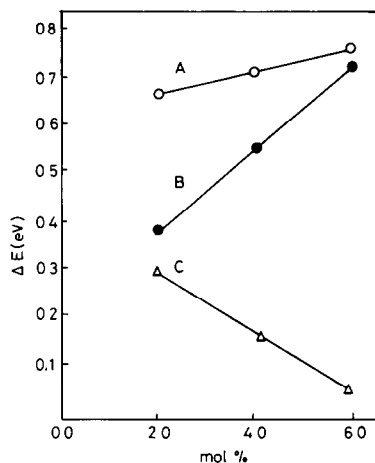


Fig. 4. An illustration showing the variation of activation energy for defect mobilities (B) before and (A) after γ irradiation, together with the variation of activation energy for carrier liberation, ϕ eV (C) as a function of mol% of lanthana in zirconia refractories.

increasing mol% of dopant which could be ascribed to the interaction of ionizing radiation with dopant and/or zirconia lattices. But the activation energy for carrier liberation decreases sharply with increasing mol% of dopant which is of great importance in industry and engineering.

In conclusion, it is of interest to note that ionic crystals crystallize in simple structures of high symmetry, because directional covalent bonding plays only a small part. In the present doped zirconia crystals, the packing of ions is dictated almost entirely by the requirements of the electrostatic forces and the relative size of ions. This kind of binding leads to considerable freedom from lattice defects, since there are no directional bonds to be ruptured or reformed when these entities migrate. Consequently, in the crystals studied in the present work, doped zirconia crystals (ionic crystals) may accommodate extensive disorder without exhibiting excessively large structural effects. The effects of disorder migrate to a large extent, by clustering and recombination of defects during and subsequent to the irradiation. For the mechanism of defects generation in ionic crystals, Seitz [11] suggested that excitons, electrons and holes produced by the absorption of electromagnetic radiation recombine and give up their energy in perturbed regions in the crystals. If this energy is released in the vicinity of a dislocation jog, cationic and anionic vacancies may be formed.

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