

Evaluation of the electrical properties of Gd₂O₃-stabilized ZrO₂ at two representative temperatures

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Zirconia doped with ceramic oxides such as CaO, Y₂O₃ and Gd₂O₃ is a good structural material and a well-known ionic conductor. In the present study the electrical properties of gadolinium oxide doped zirconia at different temperatures were studied. The results show that the maximum conductivity of Gd₂O₃ stabilized zirconia can be obtained by adding 10 mol% of Gd₂O₃, which is necessary to form a fluorite type solid solution. Finally the electrical conductivity mechanism in zirconia which has been stabilized by adding different types of dopants is discussed.

Key words: ZrO₂, Gd₂O₃, Electrical properties, Temperature, Correlation factor.

Introduction

Because of the extensive applications of zirconia, much research about its properties has been done in the past years [1-4]. Many interests have been focused on dielectric films with high permittivity as a replacement for silicon oxide in the microelectronics industry. Nowadays studies are focused on zirconia thin films as a possible key material in modern complementary metal-oxide semiconductors and even dynamic random access memory devices [5]. Zirconium oxide is an insulating material with a wide energy gap which is independent of its production technique and belongs to a group of amorphous metal oxides which exhibit bistable impedance phenomena.

A layer of zirconia between two metal electrodes forms a sandwich structure device and can be switched reversibly from a low to high impedance state and also, show a voltage-controlled negative resistance. In order to gain an understanding about transport mechanisms of the material, this characteristic of zirconia is very interesting [6].

Zirconia has a high ionic conductivity and the high stability of doped zirconia makes it ideal for use in oxygen sensors and fuel cells. It is established a phase change take place from a monoclinic to a tetragonal structure at 1150 °C and so a huge disruptive volume change happens in the material structure [6, 7]. Adding particular amounts of divalent or trivalent oxides such as CaO, Y₂O and Gd₂O₃ is a common method to

stabilize zirconia [8-12].

As reported by Butler and Bonanos, the electrical conductivity of different stabilizers approximately follows the Yb₂O₃ > Gd₂O₃ > Y₂O₃ > CaO > MgO sequence [13]. Since, the electrical properties of Gd₂O₃ and Y₂O₃ doped zirconia have not been studied as extensively as those of ZrO₂ and Y₂O₃ ceramics, because Y₂O₃ and Gd₂O₃ stabilized zirconia ceramics are very hard to prepare by the mixed oxides method. A few authors have measured the electrical properties of ZrO₂/Gd₂O₃ ceramics and single crystals [14-17]. All of these experiments except one, have been done at very high Gd₂O₃ contents, even more than 20 mol.%.

Kang *et al.* [14] have measured the electrical conductivity of 10, 12.5 and 15 mol.% Gd₂O₃ specimens. They found that the conductivity would increase with decreasing Gd₂O₃ content at temperatures up to 831 °C in an air atmosphere. It has been discovered that the conductivity of single crystals is higher than that of polycrystals. With a precise study of phase diagrams it can be seen that to avoid a heterogeneous phase distribution, addition of approximately 8-32 mol.% Gd₂O₃ to zirconia will form a fluorite type solid solution phase [18]. In this study 10-30 mol.% Gd₂O₃ was added to ZrO₂ to ensure that a homogeneous phase would form. It has been observed that incorrect data may be obtained between 8-10 mol.% Gd₂O₃ because of phase boundaries and the possible existence of a heterogeneous phase structure. Stabilized zirconia has wide possible applications such as making solid electrolytes in high temperature fuel cells and recently it has been used as an oxygen gas sensor [19]. With a high electrical conductivity, stabilized zirconia can also be used as an electrical heating element in an oxidizing atmosphere at high temperatures.

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Experimental Procedures

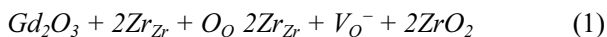
Gd_2O_3 with a high purity (99.999 wt.%) was obtained from Rasmus and Co. and purified zirconia was obtained from commercial grade with recrystallization. From primary blending of ZrO_2 and Gd_2O_3 with isostatic pressure (up to 294205 kPa), cylindrical samples were prepared. After sintering, the samples were machined precisely to have a diameter of about 35 mm. After machining, two holes were made in the middle of the samples with 4 mm distance between them to place the electrodes in them. The samples had been pre-sintered for 20 hrs at 800 °C and then a final sintering process was carried out for 24 hrs at 1750 °C or for 16 hrs at 1900 °C. The time and temperature of the sintering process depend on type of measurements. Electrodes were made from Pt-40Rh or Ir-60Rh at temperatures up to 1700 °C and 2000 °C, respectively. The samples densities were more than 99% of the theoretical value after final sintering and all original data were gathered with a PDP 11 computer system for further processing.

To determine the electrical conductivity of the material at different temperatures, conventional four point probe method was used first in a molybdenum (Mo) furnace and then in a household furnace with stabilized ZrO_2 heating elements with temperatures up to 1800 °C and 2000 °C, respectively. Samples temperatures were measured using a Pt-18Rh thermocouple at relatively low temperatures and an optical pyrometer for high temperatures.

Results and Discussion

Fig. 1 illustrates the conductivities values of samples as a function of temperature for specimens with different amounts of Gd_2O_3 . It has been observed that as the Gd_2O_3 content increases, the electrical conductivity decreases consequently. To avoid any error in measurement, because of the existence of another phase, when the amount of Gd_2O_3 is less than 10 mol.%, the conductivity of samples below 10 mol.% of Gd_2O_3 has not been measured.

With the addition of certain types of dopants in stabilized zirconia, oxygen vacancies will appear in the anionic part of its lattice and due to this, the electrical conductivity mechanism in stabilized zirconia can be explained. Oxygen ionic mobility is responsible for the high electrical conductivity observed in this study. A crystalline lattice of the fluorite type can be formulated as follows:



The electrical conductivity at very low partial pressures of oxygen is present as well as at high partial pressure. At a high oxygen partial pressure, stabilized zirconia

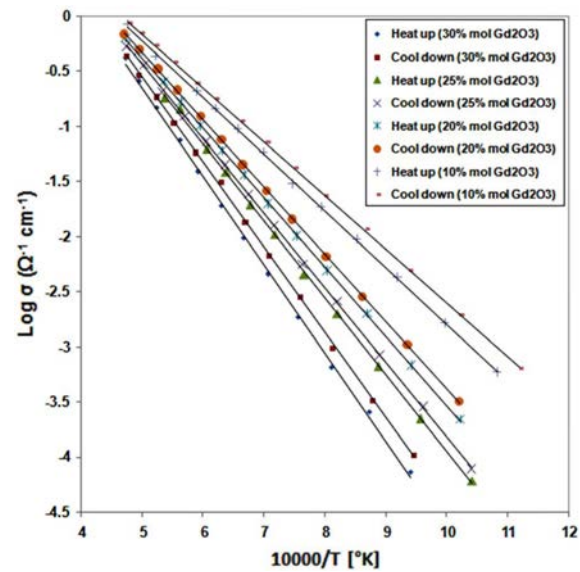


Fig. 1. Conductivity-Temperature behavior of stabilized ZrO_2 with different amounts of Gd_2O_3 .

exhibits predominantly *p*-type electronic conduction but as the oxygen pressure decreases it exhibits a considerable amount of ionic conduction. At a low pressure of oxygen at high temperatures, the conduction then becomes *n*-type electronic.

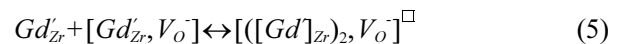
$$\sigma = \sum_i C_i Z_i U_i \quad (2)$$

where C_i is the concentration of charge carriers with charge Z_i and mobility U_i .

The vacancy concentration $[V_O^-]$ will remain approximately constant over a wide range of oxygen partial pressures:

$$[V_O^-] \approx [M_O, M_2O_3] \approx \text{Constant} \quad (3)$$

In some cases, the value of σ determined by Eq. (2) is smaller than the experimentally measured value. This is because of the formation of associates. So due to the interaction of $[V_O^-]$ and cationic defects, complexes can be formed in the ZrO_2 - Gd_2O_3 system. This can be written as follows:



The existence of such associates can be established by determining the correlation factor from the diffusion coefficient D_i and D_i can be determined from the electrical conductivity. The interaction of Gd'_{Zr} and V_O^- will become negligible hence they exist in very low concentrations. D_i is calculated from "Nernst-Einstein" equation:

$$D_i = \sigma_i \frac{RT}{C_i} \times \frac{1}{(Z_i F)^2} \quad (6)$$

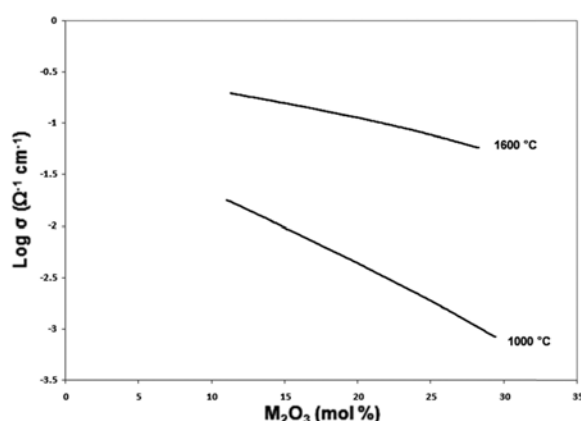


Fig. 2. The values of electrical conductivity as a function of Gd_2O_3 concentration at 1000 °C and 1600 °C.

From Eq. 2:

$$D_i = \frac{RT}{C_i} \times U_i \quad (7)$$

Fig. 2 shows the values of electrical conductivity as a function of Gd_2O_3 concentration at temperatures from 1000 and 1600 °C. In all experiments, the highest electrical conductivity was established to be in the lowest part of the fluorite type in the phase diagram. This indicates that an increase in V_{O}^- and cationic defects will result in the formation of the above mentioned associates. As the associate concentration becomes higher, the determined D_i in Eq. (7) has to be lower; hence the total conductivity becomes lower.

Conclusions

The electrical properties of Gd_2O_3 doped zirconia were investigated. Experiments show that with an increasing dopant concentration, the resistivity increases consequently. This phenomenon can be explained by the formation of particular types of associates in the

crystal structure. Eventually, these associates are complex forms and they exist due to the interaction of V_{O}^- and cationic defects.

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