Solid electrolytes based on \{1 – (x + y)\}ZrO\(_2\)-(x)MgO-(y)CaO ternary system: Preparation, characterization, ionic conductivity, and dielectric properties

Nazli Zeeshan, Rafiuddin

Physical Chemistry Division, Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

Abstract

Different composition of composite material of zirconium dioxide co-doped with magnesium oxide [MgO (x)] and calcium oxide [CaO(y)] according to the general molecular formula \{1 – (x + y)\}ZrO\(_2\)-(x)MgO-(y)CaO were prepared by co-precipitation method and characterized by different techniques, such as XRD, FTIR, TG-DTA, and SEM. Co-doping was conducted to enhance the ionic conductivity, as mixed system show higher conductivity than the single doped one. Arrhenius plots of the conductance revealed that the co-doped composition “6Mg3Ca” has a higher conductivity with a minimum activation energy of 0.003 eV in temperature range of 50–190 °C. With increasing temperature, dielectric constant value increased; however, with increasing frequency it shows opposite trend. Co-doped composition C\(_2\) exhibit higher conductivity compared to C\(_3\), owing to the concentration of Mg content (0–6%); the conductivity decreases thereafter. Zirconium oxide was firstly used for medical purpose in orthopaedics, but currently different type of zirconia-ceramic materials has been successfully introduced into the clinic to fix the dental prostheses.

Introduction

The problem associated with liquid electrolytes in practical applications, such as leakage, low energy, limited operating tem-
perature range, and low power density are removed by solid form of electrolytes [1]. Solid electrolytes have become a widely studied field of solid state chemistry in recent years, due to their excellent suitability as electrically conductive material at high temperature. The most used solid electrolyte or fast ion conductor at present are those where oxygen ions are the charge carriers; namely oxide ion conductors. Oxide ion conductors aroused worldwide attention for its wide application domains as chemical sensor, solar cells, and oxygen separation membrane and in SOFCs [2]. The classical ion conducting oxide material are those based on ZrO₂, CeO₂, and ThO₂. Recently, doped ZrO₂ was the most studied solid ionic conductor, because of its attractive anionic conductivity, as well as good thermal stability. At room temperature, zirconium dioxide having monoclinic structure, which undergoes transformation as the temperature increases. From 1170 °C to 2370 °C, zirconia has tetragonal modification whereas at a temperature higher than 2370 °C, it adopts cubic structure [3,4]. Pure zirconia is basically a poor oxide ion conductor at lower temperature. Therefore, researchers are concentrating to develop a new material where high temperature ZrO₂ cubic/tetragonal (high ionic conductivity) phases stabilized at lower temperature by doping [5]. It was observed that the stability of the high temperature modifications of zirconia with oversize divalent or trivalent cation dopants (such as V³⁺, Ca²⁺, Mg²⁺, Ce³⁺) was much higher than that of undersized trivalent cation (such as Al³⁺, Fe³⁺ and Cr³⁺) dopants. Thence, cations used as dopant for stabilization of zirconia must have a large ionic size and lower charge state than Zr [6].

The effect of the dopant oxide on the ionic conductivity of ZrO₂ based ternary system has been investigated extensively. It was reported that mixed oxides produced material with superior properties than single component [7–10]. Therefore co-doping was carried out using suitable fluorite stabilizer oxide (MgO, CaO, Y₂O₃, and CeO₂) to improve stability as well as promoting the formation of defects. In the present investigation, calcium and magnesium oxides are chosen as a dopant; not only because they are relevant to the oversized cations and are of lower charge state but also they are cheap precursors [6]. For doping of zirconium dioxide, different methods, such as co-precipitation [11] alkoxides [12], citrate routes, and powder mixing [13] are used. The present study reports the synthesis of CaO/MgO doped Zirconia and its characterization using various analytical techniques.

Experimental

Synthesis of zirconium dioxide was carried out using zirconium oxychloride (CDH, New Delhi, India) by co-precipitation method. Weighed amount of zirconium oxychloride (ZrOCl₂·8H₂O) was reconstituted in distilled water and stirred well. After obtaining homogeneous solution, precipitation was conducted by adding 100 mL of NaOH. The obtained precipitate was washed several times with distilled water until it become neutral and then placed in oven for drying at 200 °C for 3 h. The obtained raw material was grounded in an agate mortar in the medium of acetone with intermittent grinding into fine powder and heat at 800 °C for 24 h. For synthesis of Mg and Ca doped zirconia, requisite amount of precursors zirconium oxychloride, magnesium nitrate (Merck, Mumbai, India), and calcium nitrate (Otto Kemi, Mumbai, India) were dissolved in water and the above described procedure was carried out [14].

The X-ray diffraction data of the resultant material were collected in the range of 20 °C to 80 °C using Bruker AXD D8 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature for confirming the desired phase of samples. Scanning Electron Microscope (JEOL JSM-6510 LV) was used to evaluate the surface morphology features at an accelerating rate of 20 kV.

The thermal decomposition of synthesized material was analysed through thermo-gravimetric and differential thermal analysis (TG/DTA) using “PerkinElmer Thermal Analyser” with heating rate of 20 °C min⁻¹ from the temperature range of 40–800 °C in nitrogen flowing atmosphere. FTIR analysis was conducted by “Perkin Elmer Spectrum Version 10.400” in the wavelength range of 4000–400 cm⁻¹ at room temperature. The finally obtained fine powder was pelletized by applying pressure of 5 tons cm⁻². The prepared circular pellet has the radius 0.65 cm and thickness 0.1 cm. Before performing the electrical and dielectric measurements, opposite surfaces of the pelletized sample were coated by carbon paste to ensure good electrical contact with electrode capacitor. The temperature dependent electrical conductivity and dielectric measurements of the sample have been performed using a Wayne Kerr “43100” LCR meter from 30 °C to 1000 °C temperature range. The heating rate of the sample was controlled by Eurotherm C-1000 [15]. Different compositions of material used in this study are presented in Table 1.

Results and discussion

The purity and phase crystallinity of the prepared composite samples were confirmed by XRD analysis. The representative XRD patterns of synthesized material by co-precipitation method and annealed at 800 °C for 24 h was shown in Fig. 1. It can be clearly seen from the Fig. that two phase nature of the composite has been obtained and doping of MgO and CaO has no effect on the peak position, rather it only affects the peak height of pure zirconia. Phase composition analysis reveals that pure ZrO₂ (C₅) show co-existence of monoclinic and tetragonal phase; the monoclinic phase concentration was more than that of tetragonal phase. The observed diffraction pattern of pure ZrO₂ having tetragonal crystal structure with lattice constant a = 0.5364 Å, c = 0.5176 Å and monoclinic phase with lattice cell parameter a = 0.5144 Å, b = 0.51964 Å and c = 0.51964 Å [16]. Additionally some new peaks detected in case of composite diffractograms (C₁, C₂ and C₃) have a lattice constant a = b = c = 0.4195 Å, which allocates the presence of cubic structure of MgO [17]. After co-doping of zirconia with CaO and MgO (C₅, C₆) monoclinic phase of zirconia become the minor one and the high temperature cubic phase whose intensity increases as the doping level of CaO increases is the dominating one with same position of peak. However, the peaks of sample C₄ become broad with increasing concentration of CaO and fully cubic stabilized zirconia ceramics was obtained after addition of 12 mol% CaO. That was due to the decrease in grain size. Along with cubic phases, at 2θ = 31.29° and 45.15°, extra peaks of CaZrO₃ are also observed [6].

FTIR spectra for pure and composite samples were presented in Fig. 2. The observed strong absorption peak at approximately 452 cm⁻¹ region is due to 2r–O vibration, which confirmed the formation of ZrO₂ structure; prominent peak at 1383 cm⁻¹ corresponds to the O–H bonding. The peak at 1621 cm⁻¹ may be due to adsorbed moisture and broad band around 3346–3433 cm⁻¹ are due to stretching vibrations of the O–H bond of water molecules [18,19]. Further, composition C₁, C₂, C₃, and C₄ have some new IR bands at different wave numbers corresponding to MgO and CaO content. The absorption peaks at 1635 cm⁻¹ and 1137 cm⁻¹, 1012 cm⁻¹ of spectra C₁, C₂, C₃ corresponding to bending vibration of OH bonds and Mg–OH stretching vibration, respectively. The peaks around 833–617 cm⁻¹ were assigned to different Mg–O–Mg vibration modes of MgO [20,21]. The peak at 595 cm⁻¹ is associated with the vibration of Ca–O bonds. The transmission peak in spectra of C₂, C₃, and C₄ located at 876 cm⁻¹ is related to symmetric stretching vibration of Ca–O–Ca bonds. The sharp
and intense peak at 1410 cm\(^{-1}\) was assigned to the asymmetrical stretching vibration of OH–Ca [22].

The DTA curves for pure ZrO\(_2\) and its composite were illustrated in Fig. 3. The thermogram of pure ZrO\(_2\) indicates a broad endothermic peak at temperature 70\(^\circ\)C, which is due to evolution of absorbed water from the prepared powder. With increase in temperature, sharp exothermic peak was observed at 475\(^\circ\)C that was related to the lower temperature phase transition of pure ZrO\(_2\) to tetragonal/cubic phase (high temperature phases). However, for doped samples the intensity of exothermic peaks increases and peaks shifts to higher temperature, the shift increases with increase in conductivity [23–25].

Electron microscopy is a versatile tool capable of providing structural information over a wide range of magnification. SEM micrograph of undoped and doped zirconia samples prepared via co-precipitation method was shown in Fig. 4. The SEM image (a) of pure zirconia clearly demonstrate that powder consist of irregular shape agglomerates covered by smaller particles [26]. After substitution of Mg to ZrO\(_2\), smooth and uniform surface was obtained. It can be seen clearly from the image that magnesium oxide has been mixed properly with zirconium dioxide phase and form a homogeneous mixture. The particles are closely packed together and form hard agglomerates on addition of Ca and therefore conductivity of the composite decreases, within the grains formation of isolated micro pores were also observed [27]. The EDX spectra of (b) and (c) indicate the presence ZrO\(_2\), MgO, and CaO, however existence of Cl was also noticed as impurity, which may be due to entrapped unreacted chlorides of zirconium during precipitation process [28].

The technique of AC impedance is well suited for the measurement of oxide ion conductivities of solid materials. Two point probe AC measurements were carried out in frequency range of 20 Hz to 1 MHz at an applied voltage of 1V. Impedance graph involve plotting of the imaginary part (Z'') against the real part (Z'). Fig. 5 shows the complex impedance plots for two compositions C\(_2\) and C\(_3\) at temperatures 300 \(^\circ\)C, 400 \(^\circ\)C, and 500 \(^\circ\)C. Impedance spectra of the composites shows a single semicircle with vertical spike, indicating that the electrode are probably blocked and therefore electronic conduction is negligible or small compared to the magnitude of ionic conductivity. Single semicircle at

### Table 1
The nominal composition of the investigated samples.

| Sample Denotation | Sample Composition (mol%) |
|-------------------|---------------------------|
|                   | ZrO\(_2\) | MgO | CaO |                  |
| ZrO\(_2\)         | 100      | 0   | 0   | C\(_0\)          |
| 8Mg               | 92       | 8   | 0   | C\(_1\)          |
| 6Mg\(_3\)Ca       | 91       | 6   | 3   | C\(_2\)          |
| 4Mg\(_6\)Ca       | 90       | 4   | 6   | C\(_3\)          |
| 12Ca              | 88       | 0   | 12  | C\(_4\)          |

Fig. 1. X-ray diffraction patterns for the C\(_0\), C\(_1\), C\(_2\), C\(_3\), C\(_4\) composite solid electrolyte.

Fig. 2. FTIR spectra for the C\(_0\), C\(_1\), C\(_2\), C\(_3\), C\(_4\) composite solid electrolytes.

Fig. 3. DTA peaks of the C\(_0\), C\(_1\), C\(_2\), C\(_3\), C\(_4\) composite solid electrolyte.
high frequencies region was attributed to the bulk properties of the material, whereas the inclined spike is the characteristic of the impedance of oxide ion electrode electrolyte reaction. It was observed from the plots that as the temperature increases the diameter of these semi circles become smaller and resistivity decreases, which ultimately increases ionic conductivity [29,30]. It has to be noted that the complex impedance plot for composition C2 exhibit lower value of resistivity at constant temperature compared to composition C3. This is because resistivity decreases with increasing concentration of Mg and maximizes at lower concentration of Ca. Fig. 6 represents the Arrhenius plots of oxygen ion conductivities for pure and doped samples. Ionic conductivity of samples is expressed by an Arrhenius equation as

$$\sigma_T = \sigma_0 \times \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (1)

where $\sigma_T$ is the total conductivity, the pre-exponential factor is $\sigma_0$, activation energy is denoted by $E_a$, and $k$ is the Boltzmann constant [31]. At lower temperature, pure ZrO2 was not a good oxide ion conductor; for conductivity enhancement anionic vacancies are promoted by doping [32]. Above 190 °C, the drop in the conductivity was observed due to collapse of fluorite framework. This supports the argument of lattice collapse, as reported earlier [33]. Co-doped sample shows a significantly higher conductivity and outperformed the single doped and undoped ones. The conductivity obtained for C2 sample (6 Mg3Ca) is higher than C3. This is because grain boundary conductance increases as Mg content increases and maximizes at relatively lower concentration of CaO [34]. From the graph, it has been observed that the conductivity of Mg doped Zirconia (C1) is higher than Ca-doped ZrO2 (C3), owing to small ionic size of Mg compared to Ca. The high ionic radius of Ca results in blockage of oxide ions mobility, due to which conductivity decreases [35]. A second rise in the conductivity above 450 °C indicates phase transition in ZrO2 because on doping with aliovalent cation high temperature phase transition are maintain at lower temperature [24]. Linear regression method was used to calculate activation energy at low and high temperatures as presented in Table 2. The decrease in activation energy was observed from 0% to 6% increases in the content of MgO; owing to doping production of oxygen vacancies, which make ionic conduction easier.

Dielectric constant expressed the extent of distortion or polarization of electric charge distribution in the material as a function of frequency of applied electric field and is given as

$$\varepsilon = \frac{11.3Ct}{A}$$  \hspace{1cm} (2)

where capacitance in Farad is expressed by $C$, t is pellet’s thickness, and surface area of pellet is given by $A$. Fig. 7a shows a variation of dielectric constant with temperature at 1 MHz for doped samples. The highest dielectric constant was observed for the composition C2, which is slightly higher than composition C3. A significant increase in defect site and dipole takes place with increase in concentration of dopant. Dielectric constant first increases to 100 °C temperature and then decreases, above 150 °C it slightly increases till 300 °C and than rapidly increases with increase in temperature, due to increase in oxide ion mobility through solid electrolyte, this process was thermally activated. The same pattern of plot was obtained for dielectric constant as observed for conductivity [36]. Increase in temperature results in increasing value of dielectric constant, which attribute to the onset of dipole in the composite sys-

Fig. 4. SEM images of (a) ZrO2, (b) 8Mg, (c) 12Ca.
tem that create a suitable path for migration of ions. Additionally, it indicates the space charge polarization near interfaces of grain boundary [37], which results in large dielectric constant value of composite material at high temperatures [38].

Fig. 5. Impedance spectra for the C0, C1, C2, C3, and C4 composite solid electrolytes.
The value of dielectric constant also varies when plotted against different frequencies at constant temperature. Fig. 7b illustrates the plot of logarithmic $\varepsilon$ vs. frequency for the composition 6Mg3Ca. It shows the highest value for dielectric constant and conductivity when calculated in respect to temperature. However, with respect to frequency, dielectric constant shows a decrease in values as the frequency increases, due to lower polarization. In temperature range 300–550 °C, there is a sharp increase in the value of $\varepsilon$, which might be due to space charge polarization in the materials [39].

The electrical modulus formalism of solids having ion conductivity are widely analysed in term of electric modulus ($M$), and is the reciprocal of dielectric constant and was used to investigate the space charge relaxation process. The electrical modulus spectrum represents the measure of the distribution of ion energies and it also describes the electrical relaxation and microscopic properties. The electrical modulus has been calculated using the following relation

$$M = \frac{1}{\varepsilon}$$

Fig. 8 shows the electrical modulus at different frequencies as a function of temperature for the 6Mg3Ca composition.

### Conclusions

Zirconia based solid electrolyte with general formula \((1 - (x + y))\text{ZrO}_2-(x)\text{MgO}-(y)\text{CaO}\) have been synthesized with the...
help of co-precipitation method. Impedance graph consist of single
semicircle with a spike. Semicircle in high frequency region
indicates the bulk resistance value and spike in lower frequency
attributed to the oxide ion conductor electrode electrolyte
reaction. The co-doped composition “6Mg3Ca” have higher con-
ductivity compared to “4Mg6Ca”. In lower temperature region, $C_{2}$
composition show minimum activation energy of 0.003 eV, which
confirm that this composition has higher charge mobility within
this range of temperature. With increment of frequency, dielectric
constant value decreased and with increasing temperature it
shows the opposite trend. On raising the temperature, the electric
modulus of the sample decreases while frequency was increased.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal
subjects.

Acknowledgements

We express our gratitude to the Chairman, Department of
Chemistry A.M.U Aligarh for providing the necessary facilities
and UGC, New Delhi for financial support. We are also thankful
to STIC, Cochin University for XRD and TG/DTA analysis and USIF
A.M.U, Aligarh for SEM analysis.

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