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Original Article

# Solid electrolytes based on $\{1-(x+y)\}ZrO_2$-(x)MgO-(y)CaO ternary system: Preparation, characterization, ionic conductivity and dielectric properties

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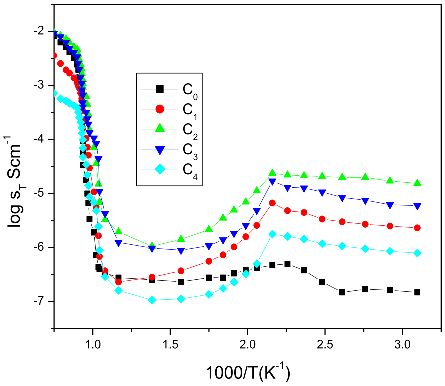
## GRAPHICAL ABSTRACT



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## 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 temperature range, and low power density are removed by solid form

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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 $ZrO_2$, $CeO_2$ and $ThO_2$. Recently, doped $ZrO_2$ was the most studied solid ionic conductor, because of its attractive anionic conductivity, as well as good thermal stability. At room temperature, zirconium dioxide has a 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 $ZrO_2$ 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 oversized divalent or trivalent cation dopants (such as $Y^{3+}$, $Ca^{2+}$, $Mg^{2+}$, $Ce^{3+}$) was much higher than that of undersized trivalent cation (such as $Al^{3+}$, $Fe^{3+}$ and $Cr^{3+}$) 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 $ZrO_2$ 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, $Y_2O_3$, and $CeO_2$) 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.

## Experiment

Synthesis of zirconium dioxide was carried out using zirconium oxychloride (CDH, New Delhi, India) by co-precipitation method. Weighed amount of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) 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 grinded 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 $20 \leq 2\theta \leq 80°$ using Bruker AXD D8 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ °A) 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 10.4.00" 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 $ZrO_2$ ($C_0$) 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 $ZrO_2$ having tetragonal crystal structure with lattice constant a = 0.35644 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 ($C_1$, $C_2$ and $C_3$) 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 ($C_2$, $C_3$), 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 $C_4$ 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 $2\theta = 31.29°$ and 45.15°, extra peaks of $CaZrO_3$ 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 Zr—O vibration, which confirmed the formation of $ZrO_2$ 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 $C_1$, $C_2$, $C_3$, and $C_4$ 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 $C_1$, $C_2$, $C_3$ correspond 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 $C_2$, $C_3$, and $C_4$ 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].

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