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Synthesis and characterization of high dielectric nano zirconium oxide

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Abstract

High dielectric constant nano zirconium oxide (ZrO_2) powder has been synthesized through a hydrothermal technique. The structural characterization of prepared sample was obtained by X-ray diffraction and showed mixed phase (orthorhombic and monoclinic). Further, the surface morphology of synthesized nano zirconium oxide (zirconia) was obtained by scanning electron microscopy (SEM). The frequency dependence of dielectric constant, dielectric loss and impedance of the sample was investigated at room temperature. Our result shows that, the dielectric constant of prepared sample is about 24 at 10^6 Hz frequency and the obtained value was approximately 3 times more than the dielectric constant of commercially available zirconium oxide.

Keywords: C. Dielectric; C. Electrical properties; Hydrothermal technique

1. Introduction

Ceramic oxides play an important role in the field of dielectric and electric applications for many years due to their unique properties such as high thermal stability, high dielectric constant, low electrical conductivity, high ionic conductivity, etc. [1]. In recent years most of the researchers focused on alternative material to silicon based dielectric devices for enhancement of storage density in dynamic random access memory, fabrication of very large scale integrated circuits and gate dielectrics for future applications [2,3]. In the view of above, zirconium oxide (ZrO_2) is one of the booming candidates due to its high dielectric constant, low toxicity, low cost and ecofriendly when compare to other ceramic oxides [4]. However, the dielectric constant of commercial zirconium oxide is nearly 7 and it is required to enhance for the fabrication of future nano scale devices as it requires high dielectric constant.

The properties of zirconium oxide based devices strongly depend on phase and crystallite size [5]. So it is essential to understand how phase and crystal size affects properties of zirconium oxide. Normally zirconium oxide exists in different phases namely monoclinic, tetragonal, cubic and orthorhombic, out of these phases monoclinic phase is stable at room temperature and gets transformed to tetragonal phase at 1170 °C. Such a transformation is accompanied with large volume changes and this leads a creation of cracks within the ZrO_2 structure. Further, as temperature increases higher than 2370 °C, zirconium oxide transforms to cubic phase. Variation of pressure also causes phase transformation of zirconium oxide for example at ~3 GPa, a Pbca-type orthorhombic phase occurs, which converts to Pnam at ~16–22 GPa [6]. Orthorhombic structure is considered to be an intermediate structure between monoclinic and tetragonal. Instead of increasing pressure and temperature, zirconium oxide in different phases can also be achieved at room temperature by adding dopants or by reducing the particle size to nano scales [7]. Nano Zirconium oxide powder can be synthesized by various methods like sol–gel, co-precipitation, hydrothermal, etc. [8–10].

In the above view, there were studies on synthesis of zirconium oxide by various precursors through various methods. They also studied dielectric properties of synthesized zirconium oxide in

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tetragonal and cubic phase [13,18]. However, existence of zirconium oxide in orthorhombic phase was rarely discussed. In present report, we have synthesized nano zirconium oxide (orthorhombic phase) through hydrothermal technique as it is an ideal technique for synthesis of ceramic oxides with high purity, controlled stoichiometry, narrow particle size distribution, controlled morphology, microstructure and high crystalinity [5].

2. Experimental procedure

Initially, appropriate amount of commercial zirconia was taken in 25 M of sodium hydroxide (NaOH) aqueous solution. This solution was mixed and stirred for one hour at room temperature and kept it in an autoclave and heated in hydrothermal reactor at 250° C for 80 h and then allowed to cool down to room temperature. After the hydrothermal treatment it took around 14 h for the whole precipitate to settle down. The resultant product was washed with dilute HCl and several times with deionised water until neutral pH was achieved. Finally it was dried in an oven at 120° C,the obtained powder was calcined at 300° C and sintered at 900° C for 2 h.

The structural characterization was obtained by X-ray diffraction (Model Rigaku ultima III). The average crystallite size (D) was also estimated according to Scherer equation

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is wavelength of the X-ray (1.54178 Å), θ is diffraction peak angle and β is full width at half maximum (FWHM) of the most intense diffraction peak, respectively. The surface morphology was obtained by Scanning Electron Microscopy (ZESIS).

To carry out dielectric measurements, the powder sample was prepared in the form of circular disk shaped pellet and then pellet was sintered and polished by fine emery paper to make the surface smooth and parallel. The silver paste coating was applied on the opposite surface of pellet as an electrode with air drying conducting silver paste and also, there by forming parallel plate capacitor geometry to have a good ohmic contact.

The frequency variation of the capacitance and dielectric loss of prepared pellets were measured by low frequency impedance analyzer (model HIOKI 3532-50) from 1 kHz to 1 MHz

The dielectric constant was calculated by using the formula

$$\varepsilon' = \frac{C\,d}{\varepsilon_0\,A}$$

where C is capacitance of pellet in pF, d the thickness of pellet, A the cross-sectional area of the flat surface of the pellet and ε_0 the permittivity for free space.

Complex impedance Z was calculated from the relation

$$Z = \frac{1}{i\omega C_0 \varepsilon}$$

where $C_0 = \varepsilon_0 A/d$, is the geometrical capacitance and ω is the angular frequency.

We have performed the same analysis for the commercial zirconia in order to compare the properties with synthesized zirconia.

3. Results and discussion

3.1. Structural and morphological studies

The X-ray diffraction (XRD) patterns of commercial zirconia and synthesized nano zirconia were shown in Fig. 1. From the figure, it is observed that the diffraction peaks of the commercial zirconia was indexed as monoclinic (P21/C) ZrO_2 (ICSD: 01-074-0815) and synthesized nano zirconia was indexed as mixed phase of orthorhombic (Pnam) and monoclinic (ICSD: 00-049-1746, 01-072-1669). Based on the X-ray diffraction, we have calculated the lattice parameters, unit cell volume and average crystallite size and they were presented in Table 1. From the table it can be seen that the unit cell volume of both commercial zirconia and synthesized nano zirconium oxide are different. It is low for synthesized nano zirconium oxide compare to commercial zirconia due to existence of mixed phase (orthorhombic and monoclinic) [11]. The estimated average crystallite size was high for synthesized nano zirconium oxide when compared to commercial zirconia and it could be due to the inter phase transformation form

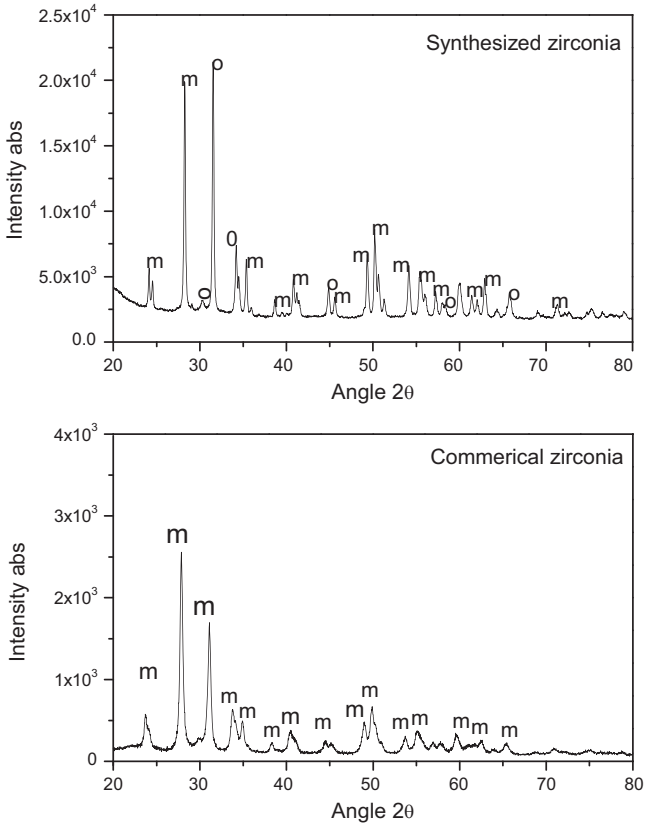

Fig. 1. XRD spectra of synthesises nano zirconium oxide and commercial zirconium oxide.