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Investigations of Impedance and Electric Modulus of ZrO_2 - TiO_2 Ceramics

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***Abstract*—ZrO_2–TiO_2 nanocrystals were prepared by co-precipitation calcination method. The formation of the composite was confirmed by X-ray diffraction. The grain morphologies were analyzed using SEM and TEM. All three morphological studies showed the formation of the composite in nanoscale. The dielectric behavior and impedance relaxation were investigated over a wide range of frequencies. The material exhibited a high dielectric constant and low loss. The ac conductivity was found to increase with increase in frequency. The high dielectric constant coupled with low dielectric loss facilitates the use of this nanocomposite for gate dielectrics.**

Keywords—Nanocomposites; Dielectric Constant; Impedance; Modulus.

I. INTRODUCTION

Mixed metal oxides have been extensively studied for their multiple applications. They exhibit high surface area, good thermal stability, and mechanical strength. Moreover high k mixed metal oxides are being used as a replacement for silica as gate dielectrics in metal oxide semiconductor devices.[1] Zirconia with its high dielectric constant, good thermal stability and low leakage current is preferred for replacing silica. In this context, the dielectric properties of Zirconium oxide and their application as a gate dielectric have been thoroughly explored[2-6] Similarly titanium oxide has also been explored for the same purpose [7-10]. Dielectric behavior of binary oxides of zirconium and titanium individually and along with lead and barium was also studied [11-13]. In this work, ZrO_2–TiO_2 nanocomposite was prepared by co-precipitation calcination technique. The morphology and properties of ZrO_2–TiO_2 were studied with a special emphasis on dielectric behavior.

II. EXPERIMENTAL PROCEDURE

A coprecipitation-calcination method was used to prepare the ZrO_2–TiO_2 nanocomposite [14]. The starting materials, zirconium oxychloride and titanium tetrachloride (AR Grade) were taken in the molar ratio 1:1 and dissolved in double distilled water. The water solution of $ZrOCl_2$ and $TiCl_4$ was treated with aqueous ammonia at a pH of 9. The resultant hydrogel was washed with water to remove NH_4Cl and dried at 110 ^{o} C for 5 hrs. The sample was further calcined at a temperature of 700^{o}C for 10 hrs. The synthesized sampled was collected and powdered for further analysis.

Morphology of the sample was studied by using a FEI Quanta FEG 200 resolution SEM and a JEOL 3010 high resolution TEM. The dielectric analysis was performed by using HIOKI 3532 LCR HIGHTESTER impedance analyzer.

III. RESULTS AND DISCUSSION

A. XRD studies

Fig.1 shows the XRD pattern of the nanocomposite. The pattern indicates that the composites were crystallized in orthorhombic phase of TiO_2 (JCPDS file 76-1937) and monoclinic phase of ZrO_2 (JCPDS file 83-0944) after calcination. The peaks indicate the presence of both the component oxides. The average particle size calculated using Debye-Scherrer formula [15] was around 30 nm.

B. SEM and TEM studies

Fig.2 shows the SEM pictograph of the nanocomposite. Well-formed nano particles with an average size of 28 nm are seen. Fig. 3 shows the TEM image along with the SAED pattern. Both the images are in good agreement with the XRD data.

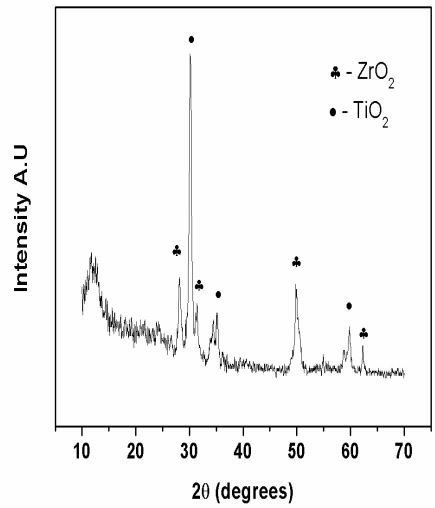

Fig. 1. XRD pattern of ZrO_2-TiO_2 nanocomposite.

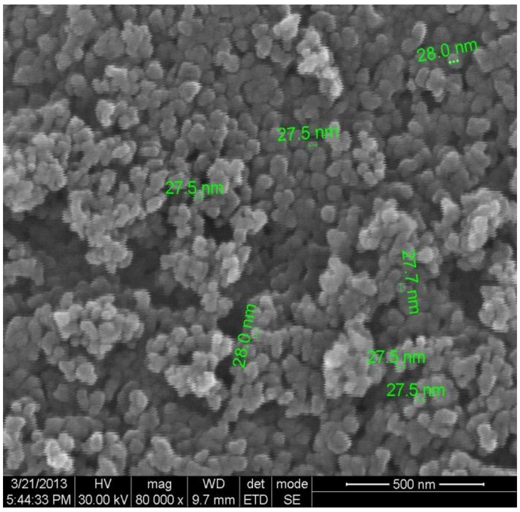

Fig. 2. SEM Pictograph of the nanocomposite.

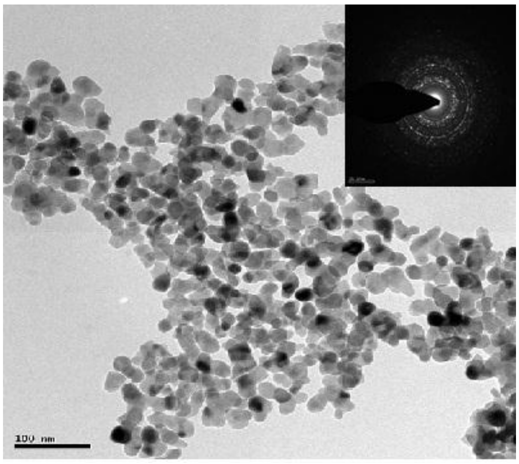

Fig.3. TEM pictograph of sample with SAED pattern as inset

C. Dielectric Studies

Fig.4. shows the variation of dielectric constant with frequency for the synthesized nanocomposite at three different temperatures. In all cases, a strong frequency dependence of permittivity, followed by a frequency independent region above 1 kHz, indicating the usual dielectric dispersion is seen. The conductivity of grain boundaries contributes more to the dielectric value at lower frequencies because the grain boundaries are more effective at lower frequencies [16, 17]. At higher frequencies the dielectric constant remains independent of frequency due to the inability of electric dipoles to follow the fast variation of the alternating applied electric field, which is the expected behavior in most dielectric materials. Therefore the permittivity is high at lower frequencies and decreases as frequency increases. Similarly, the value of permittivity increases with increasing temperature. This is due to orientation polarization of dipoles, connected with the thermal motion of molecule.

The variation of dielectric loss is shown in Fig. 5. It can be seen that loss decreases with increase of frequency.

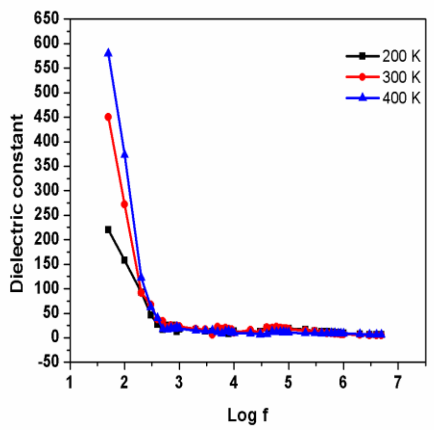

Fig.4. Dielectric constant vs log f of the ZrO_2- TiO_2 nanocomposite.

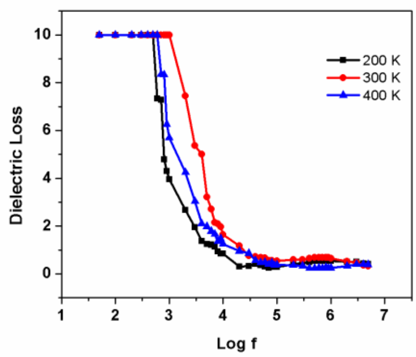

Fig.5. Dielectric loss vs log f of the ZrO_2- TiO_2 nanocomposite.

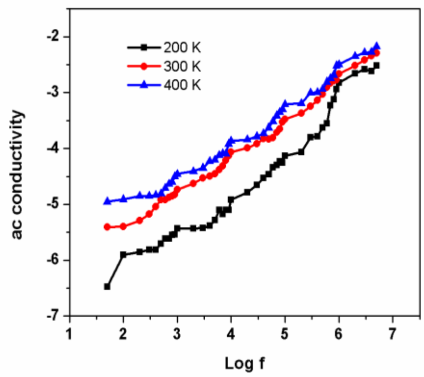

Fig. 6. Ac conductivity vs log f of the ZrO_2- TiO_2 nanocomposite

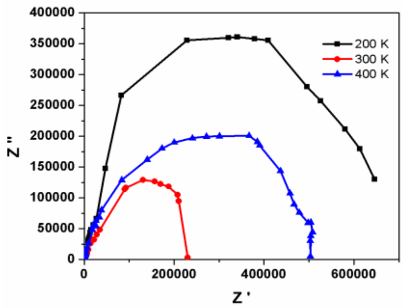

Fig. 7. Z' vs Z'' of the ZrO_2- TiO_2 nanocomposite

The frequency dependence of conductivity in the relaxation phenomenon arises due to mobile charge carriers. For a region of frequencies where the conductivity increases strongly with frequency, the transport is dominated by contributions from hopping of charge carriers among the trap levels situated in the band gap [18]. Fig. 6. shows the variation of ac conductivity with frequency.

The plot of the imaginary (Z″) versus real (Z′) parts of the complex impedance (Z*) (Cole–Cole plot) at different temperatures for ceramics is shown in Figure 7. A single arc of the impedance spectrum indicates that the electrical process in the material arises due to its bulk resistance only. The intercept of the semicircular arc on x-axis is an estimate of the bulk resistance (R_b) of the material and indicates the departure from the ideal Debye behavior. In fact, this behavior exhibits the non-Debye type of relaxation phenomenon in the materials [19].

IV. CONCLUSION

The ZrO_2-TiO_2 nanocomposite that was prepared exhibited a high dielectric constant of about 600, with a low dielectric loss for a large range of frequencies. This property of the composite makes it useful as a potential material for a gate dielectric.

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