2-D Surface Morphology and Dielectric Properties of Sr and Zr co-doped CaTiO₃

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Abstract. The ceramic sample of Ca₀.₅Sr₀.₅Ti₁₋ₓZrxO₃ where x= 0.5 and y= 0.5 (CSTZO) was synthesized by solid state reaction method. Analysis of X-ray diffraction data confirmed the formation of orthorhombic phase. The 2-D surface morphology was studied using scanning electron microscopy (SEM). The micrograph shows that the spherical shaped grains vary in the range of 1-2µm and the size of agglomerates varies in the range of 5 to 10 µm in diameter. The dielectric permittivity improved by the substitution of Sr and Zr on A and B-sites. Further, the dc conductivity measured by the two probe method in a temperature scan of 470K to 670K, showed NTCR of the material.

Keywords: Solid state reaction, dc conductivity, Surface Morphology, dielectric permittivity and SEM.

1. Introduction

A new mineral Perovskite, CaTiO₃ (CTO) was discovered by a Russian mineralogist Rose in 1839. Later, the name Perovskite was generalized and used for the ABO₃ type materials [1]. Because of its high dielectric constant and large positive temperature of the resonance frequency it has become the interesting material for researchers. These properties make CaTiO₃ to be used in microwave tunable devices, in modifying ferroelectric properties of PbTiO₃ or BaTiO₃ and in photocatalytic and communication equipment operating at microwave frequency. The modest value of dielectric loss in this material can further be lowered by substituting A-site with suitable cations [2]. Initially CaTiO₃ was prepared by the solid state reaction at high temperature (1623K) [3] with orthorhombic structure and Pbnm space group at RT [4]. CaTiO₃ and SrTiO₃ are incipient ferroelectrics with high value of dielectric constant and their solid solutions (1-x) CaTiO₃-xSrTiO₃ are widely studied as they are used in microwave dielectrics [5]. The substitution of Zr on B-site is responsible for improvement in other various properties like photocatalytic and electric activity due to change in the structure and presence of oxygen vacancies [6]. In the present studies CaTiO₃ has been used as a favourable host material and its properties are modified by doping 50% Sr at A-site and 50% Zr at B-site without affecting its parent structure. The doping atom was chosen on the basis of their valencies and ionic radii. This paper reports on surface morphology (2D), dielectric and transport properties of the Sr and Zr doped CaTiO₃ compounds in detail.

2. Experimental

The standard solid state reaction method was used to prepare Sr and Zr co-doped Calcium Titanate. The high purity calcium carbonate, strontium oxide, zirconium dioxide and Titanium dioxide were used as raw materials in stoichiometric ratio and ground in an agate mortar to mix them homogeneously followed by subsequent steps of calcinations. Finally, the powder was pelletized using hydraulic press and sintered at high temperature for 2 hours. The structural property was analysed using X-ray diffraction pattern recorded on the Rigaku Mini flex Ultima IV powder X-ray Diffractometer at a scanning rate of 5 degree/min from 20° to 90°. The Surface Morphology was
characterized using CarlZeiss EVO 18 Scanning electron microscope (SEM). The Dielectric constant was measured as a function of frequency (at RT) and as a function of temperature (from RT to 790K) in air atmosphere using HIOKI 3532-50 LCR Hi-tester. The dc conductivity of the material was measured at a constant voltage of 8V in a temperature range of 470K to 670K using a laboratory made two probe set up [7].

3. Results and Discussion
3.1. Structural property
Figure 1 shows the RT X-ray diffraction pattern of CSTZO. The observed diffraction pattern shows similarity with the ICDD file No. 22-0153 with orthorhombic symmetry. But there is a slight shift in the peak positions which can be attributed due to the doping of Sr and Zr in pristine compound. The diffractogram also shows some impurity peaks due to unreacted TiO$_2$ at 2θ position 30° and 35°.

![Figure 1. X-ray Diffraction pattern of CSTZO](image)

3.2. Surface Morphology
The 2-Dimensional SEM image has been shown in figure 2(a) and 2(b). The surface morphology shows that the grains are distributed homogeneously in the sample matrix and are almost of the same size. From the micrograph it has also been observed that due to thermal treatment the particles inter-diffuse to form clusters which lead to the densification of the material. The grain size measured from the micrograph is of the order of 1-2 μm.
3.3. Dielectric Study

The study of dielectric constant with frequency at RT is shown in Figure 3(a). From the figure it has been observed that the maximum value of dielectric constant is observed at lower frequency (10 kHz) and further increase in frequency decreases the Dielectric constant which follows the general relaxation mechanism. In the frequency region 30 kHz-200 kHz there is a dip in the dielectric constant which shows that the polarization lags behind the electric field. As the frequency increases the movement of the charge ceases because the molecules cannot respond to such high frequencies so polarization decreases and thus the dielectric constant decreases. Figure 3(b) shows the study of dielectric constant with temperature at different frequencies of 2MHz, 3MHz, 4MHz and 5MHz. Figure shows that the dielectric constant increases with increase in temperature because of increase in ionic polarization or due to oxygen vacancies which occur at high temperature [7].

Figure 3(a). Variation of dielectric permittivity (ε') with frequency at RT
Figure 3(b). Variation of dielectric permittivity ($\varepsilon'$) with temperature at different frequencies (2 MHz, 3MHz, 4MHz and 5MHz)

3.4. Transport Study
Figure 4 shows the study of log of dc conductivity with the inverse of temperature. From the figure it is clear that resistivity decreases with the increase in temperature. Here Ti$^{4+}$ or oxygen ion vacancy trap leads to thermally activated conduction via free electrons. The activation energy was calculated from linear fitting of log $\sigma$ vs. $10^3/T$ curve using the Arrhenius relation

$$\sigma = \sigma_0 \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (1)

and was found to be 0.74 eV.

Figure 4. log $\sigma$ vs. $10^3/T$ curve of sintered CSTZO pellet

4. Conclusion
The Sr and Zr co-doped CaTiO$_3$ was prepared using standard solid state reaction method. The material was characterized using X-Ray Diffraction which shows orthorhombic symmetry and a slight shift in the peak position due to the distortion caused by the doping material. The 2D surface morphology of the material shows that the grains are distributed homogeneously in the sample matrix. The high temperature dielectric study of the material indicates that the material has the high value of dielectric
constant at RT. From the DC conductivity study it is concluded that the material has negative temperature coefficient of resistance (NTCR).

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