
Structural and Dielectrical Properties of Cu Doped Barium Magnesium Zirconium Titanate Perovskite Ceramics

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Abstract: Perovskite type ceramics $(\text{Ba}_{0.9}\text{Cu}_x\text{Mg}_{0.1-x})(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ (with $x = 0.01, 0.02, 0.03$ and 0.04) relaxor composition prepared through solid state reaction route and calcination temperature is 1500°C with intermediate mixing. The room temperature XRD study suggests that all the samples have the single phase cubic symmetry with space group $pm-3m$. The pellets were sintered at 1550°C for 5 hours. Scanning Electron Microscope (SEM) observations revealed enhanced Microstructural uniformity and retarded grain growth with increasing Cu content. The dielectric study with constant frequency shows that dielectric constant increases with Cu and again decreases. Loss factor and dielectric constant decreases with increasing frequency but at very high frequencies it was independent.

1. INTRODUCTION

The perovskite ceramics family includes many titanates and is used in various electro-ceramic applications [1-3], for example, electronic, electro-optical, and electromechanical applications. By substitution of ions at A site or B site of ABO_3 can improve the dielectric properties of ferroelectric materials [4-9]. $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, PZT based ceramics has been study more than anyone else ferroelectric because of their excellent dielectric properties [10]. However, the presence of lead in those materials is about 60% in weight [11], reconsidering its use in technical applications, due its high toxicity of lead for the environment as well as for humans [12-16]. The $\text{Ba}(\text{ZrTi})\text{O}_3$ materials has due to their high permittivity [17-20] these often used as dielectrics in commercial capacitor applications [21] and is highly acceptable material for dynamic random access memory (DRAM) [22], micro electromechanical systems (MEMS) [12] applications due to its stable and high insulating characteristics against voltage [23-27]. In the composition of $\text{Ba}(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ at $y=1.5$ the three transition temperatures of BaTiO_3 , rhombohedra to orthorhombic, orthorhombic to tetragonal and tetragonal to cubic, merge near room temperature and the doped material exhibits enhanced dielectric constant. Further increasing ie $y>1.5$ the transition temperature is decreased [28, 29] and the material showed typical relaxor like behavior in $25<y<42$ [30-33]. These materials show relaxor properties at very low temperatures ie below 250K.[12]. Several attempts have been made by many research groups on these materials to shift the T_c close to room temperature. It is well known that homovalent and heterovalent substitution for barium and titanium ions give rise to various behaviours including the shifting of the transition temperature [34-36]. It was observed that a small amount of Ca substitution in the place of Ba in BZT solid solution, there is a shift in the transition temperature towards the room temperature. S.K.Rout et al [37] have reported that a amount of Mg (<1.5 atom %) substitution in the place of Barium in BZT the transition temperature decreases with increase in Mg contents. The Cu ionic radius can able to occupy the Mg ion in the centre of 12 coordinated sites. On the other hand, it may take 12 coordination sites with eight near neighbors and four more distant ones. That modification supposes a possible displacement of Cu ion out of the oxygen dodecahedron centre able to induce a dipolar moment whose occurrence should leads to increase of Transition temperature. This inspired us to work on effect of Cu on structural and Dielectrical properties of $(\text{Ba}_{0.9}\text{Cu}_x\text{Mg}_{0.1-x})(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ relaxor composition prepared through solid state reaction route.

2. EXPERIMENTAL

The perovskite samples of pure and Cu doped Barium Magnesium Zirconium Titanate (BCMZT (0.000), (0.010), (0.015), (0.020), (0.025)) were prepared by conventional solid state reaction method. The starting raw materials were BaCO₃ (Chen Chems., Chennai), TiO₂ (Loba Chem., Mumbai) and ZrO₂ (Loba Chem., Mumbai), MgO (Chen Chems., Chennai) and CuO (HiMedia Ltd. Mumbai). All the powders were having more than 99% purity. The powders were taken in a suitable stoichiometry for 20 gm of samples. The powders were thoroughly mixed in an agate mortar in dry and wet mixing with appropriate amount of Acetone for 6 Hrs. After proper mixing, mixed powders were calcinated at 1300 °C for 2 Hrs., 1400 °C for 2 hrs. and 1500 °C for 4 hrs. A small amount polyvinyl alcohol was added to the calcinated powder for fabrication of pellets, which was burnt out during high temperature sintering. The circular disc shaped pellets were prepared by applying a uniaxial pressure of $4.5 \times 10^6 \text{ N/m}^2$. The pellets were subsequently sintered at an optimized temperature of 1550 °C for 5 Hrs. A preliminary study on compound formation and structural parameters was carried out using an X-ray diffraction (XRD) technique with an X-ray powder diffractometer. The XRD pattern of the calcinated powder was recorded at room temperature PANalytical X'pert pro with CuK_α radiation (1.5405 \AA) in a wide range of Bragg's angles 2θ ($15 \leq 2\theta \leq 80^\circ$). Micro structures of sintered pellets were recorded by scanning electron microscope (SEM)(JEOM JSM-6380 LA). The pellets were then electrode with high purity air –drying silver paste and then dried at 500°C for 1Hr. Impedance spectroscopic analysis was done using Agilent E4980A Precision LCR meter with temperature (150-330K) and frequency (20Hz-200KHz).

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

Fig 1 shows the XRD pattern of the pure and Cu doped BCMZT (0.000, 0.010, 0.015, 0.020, 0.025) samples. The XRD analysis provides that the samples are having single perovskite structure. BaTiO₃(BTO) has the tetragonal structure at room temperature. The ionic radii of Ba²⁺ and Ti⁴⁺ are 1.35 Å and 0.605 Å respectively. If we doped BTO with Mg²⁺ and Zr⁴⁺ whose ionic radii are both 0.72 Å Mg occupies A site and Zr occupies B site of BTO. The pure BCMZT single phased cubic structure when the Mg content is < 1.5% at -% [38] and Zr content is < 0.42% at -%[39]. The small amount of Cu has ionic radius 0.73 Å doping to BCMZT. By doping with Cu the diffraction angles are shifted towards the lower angle side indicating the increase in lattice parameters due to the incorporation of smaller content of Cu in place of Mg.

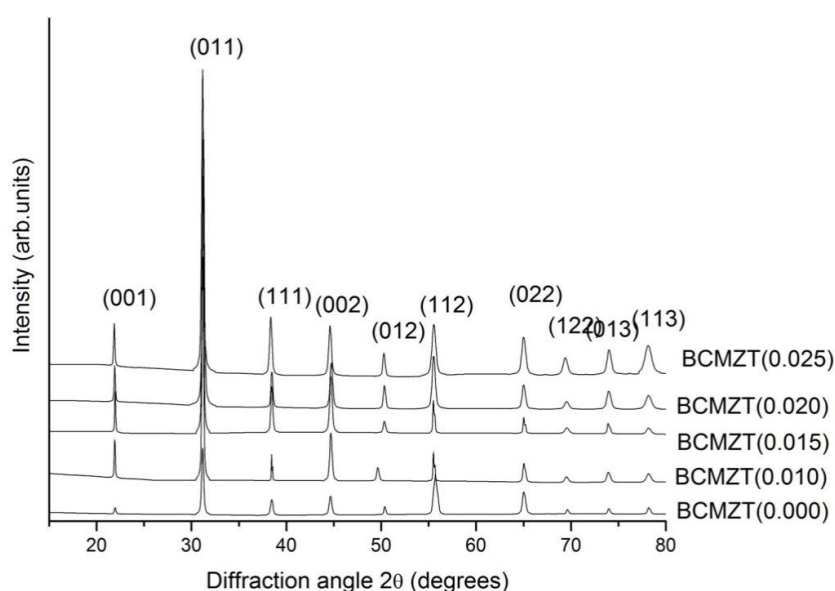


Fig1. Pure and Cu doped BCMZT (0.000, 0.010, 0.015, 0.020, 0.025) samples

3.2. Microstructural Analysis

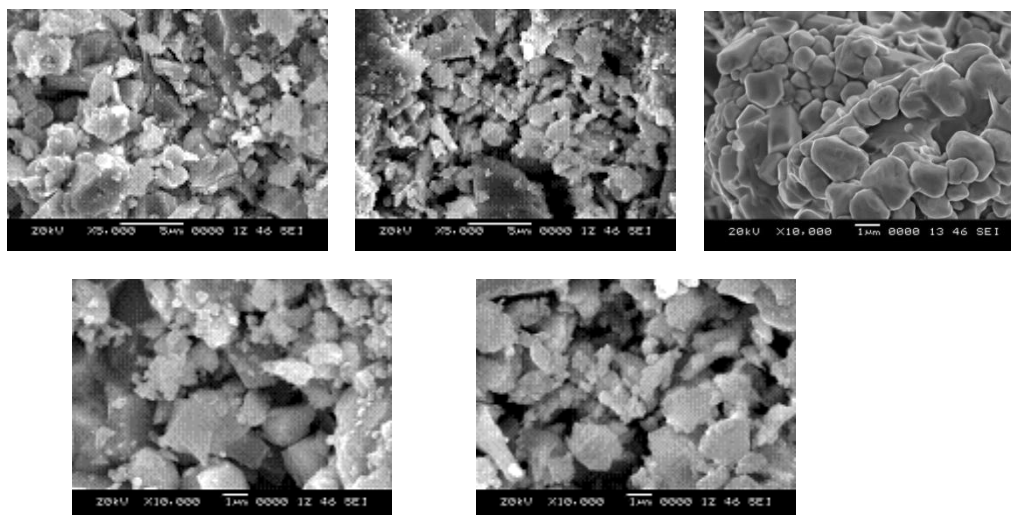


Fig2. SEM micrograph of pure and Cu dope BCMZT(0.000, 0.010, 0.015, 0.020, 0.025) samples

Fig 2 shows The SEM micrographs of pure and Cu dope BCMZT (0.000, 0.010, 0.015, 0.020, 0.025) samples. It is found that the average grain size of samples are ~ 1.66 , ~ 1.67 , ~ 1.8 , ~ 1.9 and ~ 1.98 μm as the Cu content increases from 0 to 0.025%. This increase is in agreement with our XRD pattern. Moreover the surface observation shows a good density of grains with some porosity.

3.3. Dielectric properties

3.3.1. Temperature Dependence Dielectric Properties

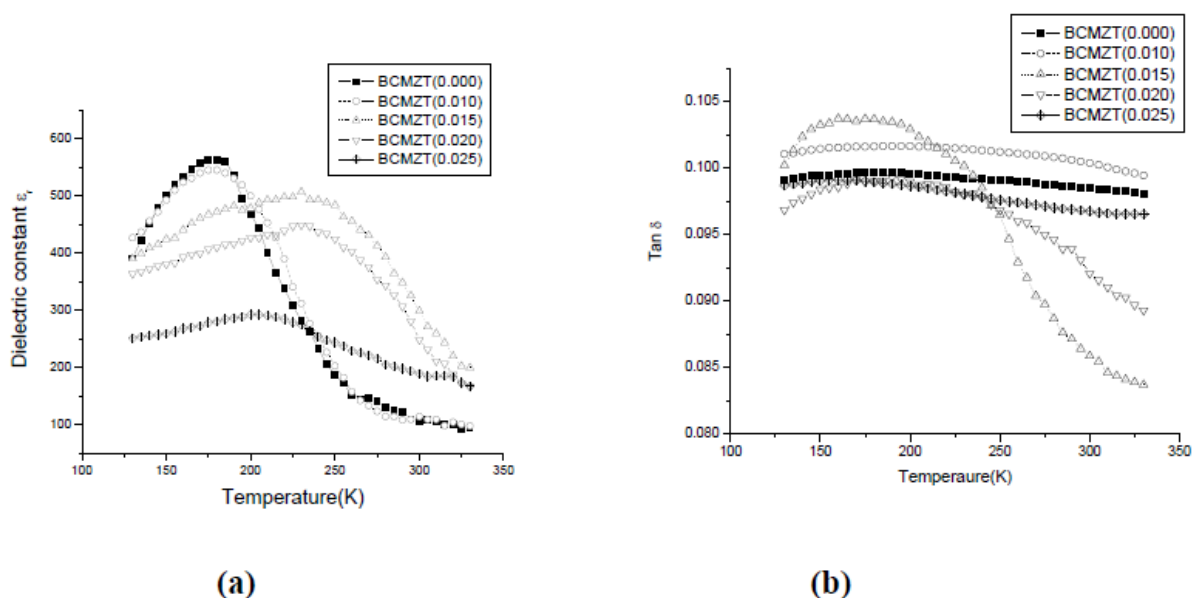


Fig3. Temperature dependence of (a) Dielectric constant (b) Dielectric loss of pure and Cu dope BCMZT(0.000, 0.010, 0.015, 0.020, 0.025) samples

Fig.3 shows the temperature dependence of the dielectric constant and loss of pure and Cu doped BCMZT samples measured at 1MHz. The figure shows, the value of dielectric constant increases gradually to a maximum value (ϵ_m) with increase in temperature up to transition temperature and then decreases indicating a phase transition. It is also found that the Curie temperature T_c of BCMZT samples with Cu dopant of (0.000, 0.010, 0.015, 0.020, 0.025) corresponding to the maximum dielectric constant is 180, 180, 230, 230 and 205 respectively. The results indicates that the curie temperature of BCMZT first increased may be due to Mg ions replaced by Cu ions and Cu ionic radius is little more, it can increase the grain size, again decrease in curie temperature is due to exactly

not joining the Cu atoms in Mg sites, due to the Cu ions conducts the little current then the dielectric constant and curie temperature both may be decreased. According to figure 3a the peak value of the dielectric constant of BCMZT samples with the Cu dopant of (0.000, 0.010, 0.015, 0.020, 0.025) is 566,545, 508, 450 and 300 respectively. The result indicates that the peak value of dielectric constant for an undoped sample is the maximum and the peak value decreases with Cu content.

Figure 3b shows that the dielectric loss initially increases with temperature reaches maximum. Further increase in temperature loss is decreased but for BCMZT samples of (0.015, 0.025) it is at lower temperature high value of loss due to the presence of all types of polarisation and may be due to the contribution of finite resistivity of the materials. Further increase in temperature increase in ionic conductivity resulting from the disordering of mobile cations in the oxygen octahedral skeleton [39].

3.3.2. Frequency Dependence Dielectric Properties

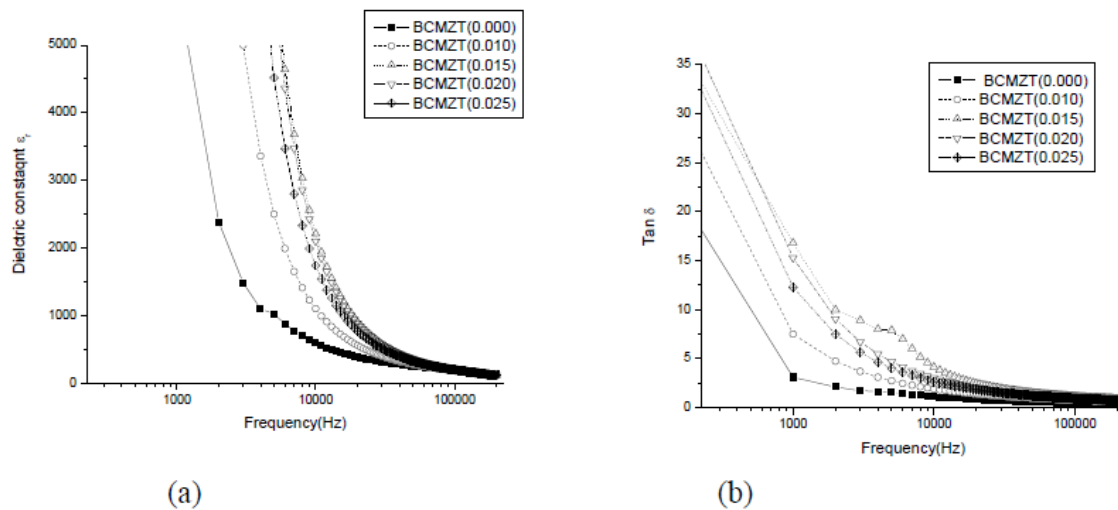


Fig4. Frequency dependence of (a) Dielectric constant (b) Dielectric loss of pure and Cu doped BCMZT(0.000, 0.010, 0.015, 0.020, 0.025) samples

As shown in Fig 4a first, it is found that the dielectric constant of BCMZT samples decreased with frequency. Second, it is also found the dielectric constant of BCMZT (0.000) decreased rapidly at low frequencies. At very high temperatures dielectric constant is very low and it maintains constant value. It may be due to there must be defects with opposite charges (dipoles) to preserve charge neutrality. These dipoles could be oriented to align the direction of the applied electric field. When the frequency increases, the dipoles do not catch up with the change of the electric field to complete polarisation so that the dielectric constant decreases [40].

In the Fig 4b the dielectric losses were a combined result of electrical conduction and orientational polarisation of the matter. The energy losses, which occur in dielectrics due to dc conductivity and dipole relaxation. The loss factor of a dielectric material is a useful indicator of the energy loss as heat.

4. CONCLUSION

Perovskite types $(\text{Ba}_{0.9}\text{Cu}_x\text{Mg}_{0.1-x})(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ (with $x=0.000, 0.010, 0.015, 0.020, 0.025$) ceramics have prepared through solid state reaction route. The room temperature XRD study suggests that the composition have single phase cubic symmetry with space group pm-3m. The dielectric study reveals that the material undergo a diffuse type ferroelectric phase transition. The transition temperature firstly increased with Cu content and further increasing it was decreased but the maximum dielectric constant decreased with Cu content.

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