



Synthesis and characterization of B-site doped BMT with Zr perovskite type compounds.

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ABSTRACT:

The perovskite samples of Barium Magnesium Zirconium Titanate ($\text{Ba}_{0.9}\text{Mg}_{1.0}(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$) is prepared by conventional solid state reaction method. The starting raw materials were BaCO_3 , TiO_2 , MgO and ZrO_2 . The XRD study at room temperature suggests that these have cubic and tetragonal symmetry phases. The behavior of the measured dielectric permittivity and dielectric loss with temperature and frequency reveals that the materials undergo a ferroelectric phase transition and are of the relaxor type. The crystal structure, surface morphology and dielectric properties of Zr and Mg doped barium titanate ceramics were investigated. Zr^{4+} and Mg^{2+} ions have entered the unit cell maintaining the perovskite structure of solid solution without the evidence of any additional phase when Mg content is 0.1 at-% and the Zr content 0.10 at-%.

KEYWORDS: Lead free ceramics, BaTiO_3 , dielectric materials, impedance, XRD, SEM.

INTRODUCTION

Lead based ceramics has been study more than anyone else ferroelectric because of their excellent dielectric properties [1]. However, the presence of lead in those materials is about 60% in weight [2], reconsidering its use in technical applications, due its high toxicity of lead for the environment as well as for humans [3-7]. Barium Titanate, BaTiO_3 (BTO) is the most common ferro electric material, which is used to manufacture electronic components such as multilayer capacitors, positive temperature coefficient thermistors, piezo electric transdures, ferro electric memory and so on, because of its excellent dielectric, piezo electric and ferro electric properties [8,9]. The micro level structure and dielectric properties of BTO can be modified by addition of the dopants such as La^{3+} , Ce^{2+} , Mn^{4+} , Nb^{5+} , Nd^{3+} , Cr^{3+} , Zr^{4+} , Mg^{2+} , Sr^{2+} and Si^{4+} to occupy Ba^{2+} on A sites or Ti^{4+} on B sites to form the solid solution [10-26]. Numerous works have also been carried out to confirm the codoping effects of rare earth oxides on the microstructure and electrical properties of $\text{BaTiO}_3\text{-MgO}$ based system [27-29]. However, there are only few works concerned with the properties of the MgO singly doped barium titanate system. A small amount of Mg substitution in the place of Ba in BZT solid solution the dielectric properties will be changed. But the transition temperature shifted towards lower temperature. S.K.Rout et al [30] 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. It has been reported that [31] at □ 15% Zr substitution in $\text{Ba}(\text{ZrTi})\text{O}_3$ (BZT) the three transition temperatures of BT, rhombohedra to orthorhombic, orthorhombic to tetragonal and tetragonal to cubic, merge near room temperature and doped material exhibits enhanced dielectric constant with further increase in Zr content beyond 15 atoms %, a diffuse





dielectric a normally in ceramic has been observed with the decrease in one transition temperature [32] and the material showed typical relaxor like behavior in the range 25-45 atom % Zr substitution [33]. Unexpectedly the lead free ceramics shows the relaxor properties at low temperatures [34]. Several attempts have been made by researchers on these materials to shift the T_c to close to room temperature. It is well known that homovalent and hetrovalent substitution for barium and titanium ions gives rise to various behaviors including the shifting of the transition temperature. This inspired to work on Structural and Dielectrical properties of Barium Magnesium Zirconium Titanate ((Ba_{0.9}Mg_{1.0})(Zr_{0.1}Ti_{0.9})O₃) perovskite composition prepared through solid state reaction route.

EXPERIMENTAL

The perovskite samples of Barium Magnesium Zirconium Titanate (Ba_{0.9}Mg_{1.0})(Zr_{0.1}Ti_{0.9})O₃ were prepared by conventional solid state reaction method. The starting raw materials were BaCO₃ (Chen Chems., Chennai), TiO₂ (Loba Chem., Mumbai), MgO (Chen Chems., Chennai) and ZrO₂ (Loba Chem., 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 using PANalytical X'pert pro with CuK_α radiation (1.5405 Å) 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. Dielectric measurement analysis was done using Agilent E4980A Precision LCR meter with temperature (150-573K) and frequency (20Hz-200KHz).



RESULTS AND DISCUSSION

3.1 Structural analysis

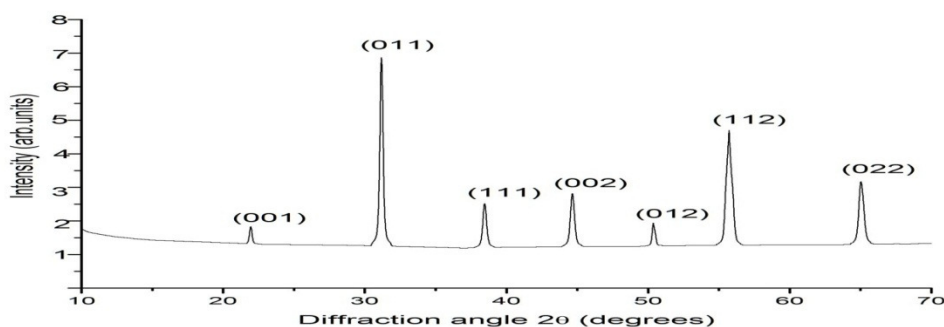


Fig.1 XRD of $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ sample.

The XRD analysis provides that the samples are having single perovskite structure. BaTiO_3 (BTO) has the tetragonal structure at room temperature. The ionic radii of Ba^{2+} and Ti^{4+} are 1.35 \AA and 0.605 \AA respectively. If we doped BTO with Mg^{2+} and Zr^{4+} whose ionic radii are both 0.72 \AA Mg occupies A site and Zr occupies B site of BTO. The pure BMT single phased tetragonal structure when the Mg content is $< 1.5\%$ at $-\%$ (9) if Zr content is $< 0.42\%$ at $-\%$ (10) the sample is changes into the cubic structure. By doping with Zr the diffraction angles are shifted towards the lower angle side indicating the increase in lattice parameters due to the incorporation of smaller content of Zr in place of Ba. In Fig.1 $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ sample has the tetragonal structure.

3.2 Microstructural analysis

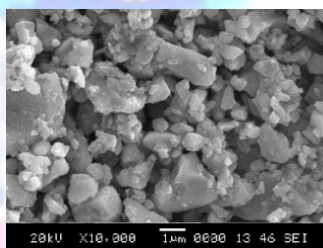


Fig 2 SEM micrograph of $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ sample.

Fig 2 shows that the average grain size of sample is $\approx 1.00 \mu\text{m}$ it is increased as the Zr content increases with compared to pure BTO compounds.. 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

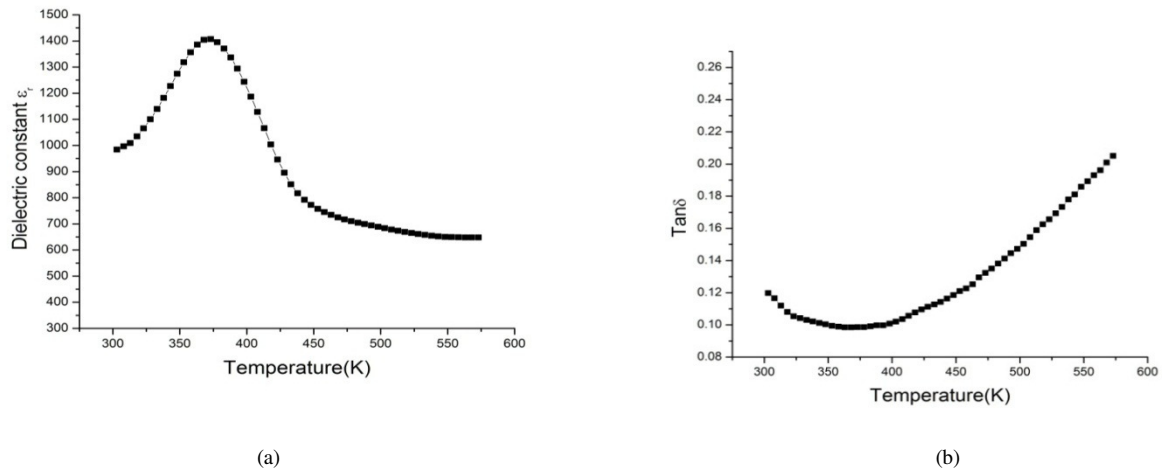


Fig 3. Temperature dependence of (a) Dielectric constant (b) Dielectric loss of $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ samples

Fig.3(a) shows the temperature dependence of the dielectric constant and loss of Zr doped BMZT sample 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 $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ sample corresponding to the maximum dielectric constant is 373. The results indicates that the curie temperature of BMZT decreased may be due to Ti ions replaced by Zr ions and Zr ionic radius is little more, it can increase the grain size and exactly not joining the Zr atoms in Ti sites, due to the Zr ions conducts the little current then the dielectric constant and curie temperature both may be decreased. According to figure 3 the peak value of the dielectric constant of sample is 1406. The result indicates that the peak value of dielectric constant decreases with Zr content.

In Figure 3(b) shows that the dielectric loss initially increases with temperature reaches maximum. Further increase in temperature loss is decreased but for $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ it is at lower temperature little bit 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 loss decreases minimum and further increasing temperature loss also increased

3.3.2. Frequency dependence dielectric properties

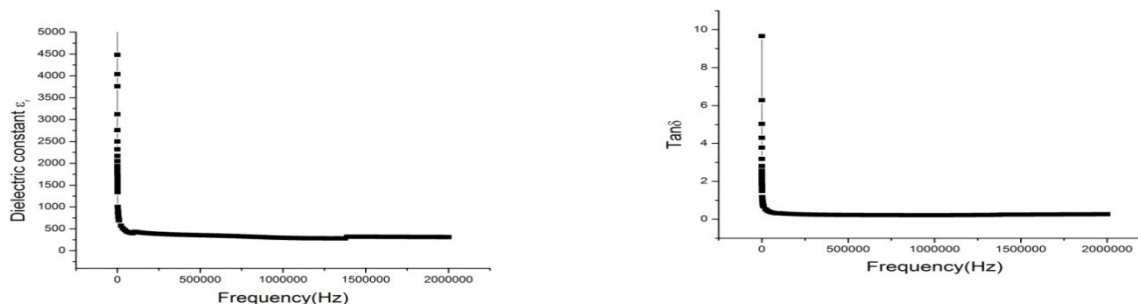


Fig 4. Frequency dependence of (a) Dielectric constant (b) Dielectric loss of $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ samples.

As shown in Fig 4a it is found that the dielectric constant of $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ decreased rapidly at low frequencies. At very high frequencies 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. 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.

CONCLUSIONS

Perovskite types $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics have prepared through solid state reaction route. The room temperature XRD study suggests that the composition of $(\text{Ba}_{0.9}\text{Mg}_{1.0})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ have single phase tetragonal structure. The dielectric study reveals that this material undergo a diffuse type ferroelectric phase transition. The transition temperature decreased with Zr content and the maximum dielectric constant also decreased with Zr content.

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