Enhanced dielectric properties of BaTiO$_3$ ceramics with cerium doping, manganese doping and Ce-Mn co-doping

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Abstract: Ba$_{1-x}$Ce$_x$Ti$_{1-y}$Mn$_y$O$_3$ (where x and y varies from 0.00 to 0.03) ceramic samples are synthesized by conventional solid state reaction technique. The samples are sintered at 1473 K for 4 h. The grain size is observed to increase with increasing dopant and co-dopant concentration. The X-ray diffraction confirmed the cubic phase of these BaTiO$_3$-based ceramics with a small amount of secondary phase. The current density shows a nearly linear relationship with voltage, and the AC resistivity of the samples is observed to decrease with increasing frequency and doping concentration. The dielectric constant and dielectric loss were observed to decrease with frequency in the lower frequency range (0.2–10 kHz), but remained almost the same at the high-frequency region (>10 kHz). Though Ce-doped samples shows better dielectric properties than Mn-doped samples, the Ce-Mn co-doped samples, having improved their dielectric properties, can be used to fabricate different optoelectric devices.

Keywords: dielectric properties; grain size; resistivity; SEM; solid state reaction; XRD.

1 Introduction

Barium titanate (BaTiO$_3$) is a ferroelectric ceramics, which has been used for many years because of its enhanced dielectric properties [1]. It exists mainly in the tetragonal symmetry and holds a dielectric constant 100 times larger than that of other insulators [2, 3], high stability, and low leakage current and electro-optic coefficient [2].

Because of its simple structure, BaTiO$_3$ can react easily with other oxides to form solid solutions and, therefore, is useful for manufacturing various electronic components [3]. Owing to extremely high dielectric constant and low dielectric loss [1], BaTiO$_3$ doped with other rare earth elements was used to fabricate multilayer capacitors (MLCs) of electro-optic devices, semiconductors, PTC thermistors, and piezoelectric devices [1–4].

BaTiO$_3$ is a member of the perovskite family having the general form ABO$_3$ [1], where A is a monovalent, divalent, or trivalent metal, and B is a pentavalent, tetravalent, or trivalent element, respectively. BaTiO$_3$ can be doped with various types of dopants in order to improve its performance, to control the grain boundaries and also the electrical properties [3]. It was observed that the grain growth during the sintering of BaTiO$_3$, and the types and concentration of the additives in it, play important roles on its dielectric properties [3, 5, 6]. Depending on the valency and the types of substituting ions, it is possible to dope BaTiO$_3$ both at the A and B sites [7]. It can be doped with trivalent ions such as cerium (Ce), lanthanum, yttrium, and antimony on Ba-ion sites or with pentavalent ions like niobium, antimony, and tantalum on Ti-ion sites [8].

Ce is the most prolific rare earth element, which exists in both 4+ and 3+ oxidation states and can be substituted on both sites of BaTiO$_3$. When BaTiO$_3$ and CeO$_2$ are sintered in the presence of air with an additional amount of TiO$_2$, Ce is incorporated as a donor at the Ba-ion sites of BaTiO$_3$ [9]. On the other hand, when sintering is operated in BaTiO$_3$ and CeO$_2$ with excess amount of BaO, Ce is incorporated at the Ti sites [9]. In some research, it was observed that BaTiO$_3$ highly doped with Ce$^{3+}$, showing propitious dielectric properties such as high permittivity and high endurance [10]. It was also reported that the addition of Ce causes the increase in grain size of BaTiO$_3$ with sharp grain boundaries and a decrease in lattice parameter, a [2]. Therefore Ce doping can cause an improvement in the various properties of BaTiO$_3$.

Manganese (Mn) can exist in Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ states depending on the oxygen partial pressure and acts as an acceptor during the substitution in the B sites of the ABO$_3$ type materials [11]. When Mn$^{3+}$ substitutes the Ti$^{4+}$ site as an isovalent dopant, it shifts the Curie point of the...
ceramics and depresses the dielectric peak [3]. Mn addition can also increase the average grain size of BaTiO₃, which reduces the AC resistivity.

By adopting the doping process, the electrical properties of the BaTiO₃ ceramics can be controlled. As Ce and Mn both have a significant role as a dopant on the properties of BaTiO₃, the effect of Ce and Mn co-doping on the various properties of BaTiO₃ was studied in this research.

2 Materials and methods

Ceramic samples with the general formula Ba₁₋ₓCeₓTi₁₋ₚMnₚO₃ (x, y = 0.00, 0.00; 0.01, 0.00; 0.02, 0.00; 0.03, 0.00; 0.00, 0.01; 0.00, 0.02; 0.00, 0.03; 0.01, 0.01; 0.02, 0.02; 0.03, 0.03) were prepared using the conventional solid state reaction technique. The raw BaO, CeO₂, TiO₂, and MnO₂ powders (Merck, Darmstadt, Germany, purity 98%) were screened and weighed appropriately, mixed and ground in an agate mortar for 15 min. Then the powders were wet mixed for 6 h using ball milling with the aid of zirconium balls having a diameter of 1 cm to form a homogeneous mixture. These mixtures were then dried and ground for 1.5 h. The samples were then calcined at 973 K for 2 h (with heating and cooling rate of 10 K/min) in a Nabertherm furnace (model HT 16/18, Bremen, Germany). The powders were again ground for 15 min and added with binder (81% C, 13.5% H, 2.9% O, and 2.6% N). Finally, these powders were pressed into pellets of thickness 2 mm and diameter 15 mm using a uniaxial hydraulic press (model HERTZOG HTP 40, series no- MA1482211, Ennepetal, Germany) with a 40-kton force and sintered at 1473 K for 4 h with a heating and cooling rate of 10 K/min. The sintered pellets were polished and used for the measurement of the structural, morphological, and electrical properties. The surface morphology and average grain size of the samples

![Figure 1: SEM images of the Ba₁₋ₓCeₓMnₚTi₁₋ₚO₃ for x, y = (A) 0.00, 0.00, (B) 0.01, 0.00, (C) 0.02, 0.00, (D) 0.03, 0.0, (E) 0.00, 0.01, (F) 0.00, 0.02, (G) 0.00, 0.03, (H) 0.01, 0.01, (I) 0.02, 0.02, and (J) 0.03, 0.03.](image-url)
were estimated by a scanning electron microscope (SEM, Hitachi S-3400N, Tokyo, Japan), and the structural property was investigated by an X-ray diffractometer (model Rigaku Ultima IV, Tokyo, Japan). For electrical measurements, high-conducting silver paste was applied on both sides of the pellets, and a Wayne Kerr 6500B series Precision Impedance Analyzer (Bognor Regis, West Sussex, UK) was used to measure the dielectric properties.

### Results and discussion

SEM micrographs of the doped and co-doped BaTiO$_3$ samples with various concentrations of Ce and Mn are presented in Figure 1A–J, where the microstructures are observed to consist of intergranular pores and grains of various sizes and irregular shapes. The grain size is measured from the SEM micrographs. For each sample, several

| Sample composition | Average grain size ($\mu$m) | Lattice parameter, $a$ (Å) | Exponent, $n$, of the $J$–$V$ curve | Dielectric constant ($\varepsilon_r$) |
|-------------------|-----------------------------|-----------------------------|-------------------------------------|----------------------------------|
| BaTiO$_3$         | 0.230                       | 4.0007                      | 1.054                               | 515                              |
| Ba$_{0.99}$Ce$_{0.01}$TiO$_3$ | 0.242                       | 4.0006                      | 0.900                               | 1051                             |
| Ba$_{0.97}$Ce$_{0.03}$TiO$_3$ | 0.290                       | 3.9991                      | 1.330                               | 219                              |
| BaTi$_{0.99}$Mn$_{0.01}$O$_3$ | 0.244                       | 4.0028                      | 1.190                               | 623                              |
| BaTi$_{0.98}$Mn$_{0.02}$O$_3$ | 0.252                       | 4.0027                      | 0.945                               | 1146                             |
| BaTi$_{0.97}$Mn$_{0.03}$O$_3$ | 0.265                       | 4.0031                      | 1.200                               | 983                              |
| Ba$_{0.99}$Ce$_{0.01}$Ti$_{0.99}$Mn$_{0.01}$O$_3$ | 0.286                       | 4.0005                      | 1.380                               | 837                              |
| Ba$_{0.98}$Ce$_{0.02}$Ti$_{0.98}$Mn$_{0.02}$O$_3$ | 0.291                       | 4.0012                      | 1.167                               | 866                              |
| Ba$_{0.97}$Ce$_{0.03}$Ti$_{0.97}$Mn$_{0.03}$O$_3$ | 0.312                       | 3.7664                      | 1.312                               | 968                              |

Figure 2: XRD pattern for the (A) pure, (B) Ce doped, (C) Mn doped, and (D) Ce-Mn-co-doped BaTiO$_3$, where the filled and unfilled circle represents the BaTiO$_3$ and BaTi$_2$O$_5$ phase, respectively.
SEM micrographs were taken to estimate the average grain size from at least 100 grains. The average grain size and lattice parameter for the different samples are presented in Table 1. It is observed that Ce doping has a significant role on the increase of grain size of the ceramics, and the grain size is the highest for 3 wt% of Ce doping (0.580 µm). However, no such sharp increase in grain size is observed for Mn doping, and therefore, it can be predicted that Mn doping cannot influence the microstructure as significantly as Ce. The increase or decrease in grain size mainly depends on the ionic radii of the substituting and parent atoms. The grain size increases if the ionic radius of the doped atom is larger than that of the parent atom and vice versa. Now in BaTiO$_3$, the Ba$^{2+}$ site is considered as the A site and the Ti$^{4+}$ site as the B site. Ce can occupy any of the sites due to its multi-valence. If Ce occupies the A site, due to having smaller ionic radius compared to Ba$^{2+}$, the grain size will decrease. However, in our case, the grain size is observed to increase, which is considered to happen due to the incorporation of Ce at the B site. Dependence of grain size distribution on a different site occupancy was described in many studies [12–15]. In a previous study, it was shown that Ce is most probably incorporated as $4^+$ on the B site and $3^+$ on the A site, and in BaTiO$_3$ with a Ti-rich phase, Ce$^{3+}$ is incorporated in the A site ion, but in the Ba-rich case, it is incorporated in the B-site ion with either $3^+$ or $4^+$ valence [12]. Therefore, it can be considered that in our case, Ce is incorporated as $4^+$ at the Ti$^{4+}$ sites rather than at the Ba$^{2+}$ sites. As Ce has a larger ionic radius compared to that of Ti$^{4+}$, the grain size become larger due to the B-site occupancy. Owing to a similar reason, the increase in grain size is also observed for the co-doped sample with the increase of doping concentration.

The XRD patterns of all the compositions of pure, doped, and co-doped BaTiO$_3$ are shown in Figure 2, indicating the cubic phase of the ceramics. The absence of splitting of the XRD peaks confirms the cubic phase of BaTiO$_3$ with a small amount of secondary phase of BaTi$_2$O$_5$, which may be due to the use of raw BaO, CeO$_2$, MnO$_2$, and TiO$_2$ during the sample preparation [2, 16, 17]. It is also observed that some secondary phases of BaCO$_3$ exist [18], which may be due to the CO$_2$ in air. However, the

![Figure 3: XRD profile around (110) peaks of the (A) Ba$_{1-x}$Ce$_x$TiO$_3$ (where $x = 0.00, 0.01, 0.02, 0.03$), (B) BaMn$_y$Ti$_{1-y}$O$_3$ (where $y = 0.00, 0.01, 0.02, 0.03$), and (C) Ba$_{1-x}$Ce$_x$Mn$_y$Ti$_{1-y}$O$_3$ (where $x = y = 0.00, 0.01, 0.02, 0.03$) samples.](image-url)
number of peaks of the BaTi$_2$O$_5$ phase decreases with the increase in concentration of the additives. The intensity of the major peak increases for the samples with Ce and Mn doping except for the samples having secondary BaTi$_2$O$_5$ phase, which indicates a better crystallization of the samples. No significant shifts in the XRD peaks are observed for the samples indicating that the structure of the samples remained almost unchanged.

Figure 3A–C shows shifting of the major peak (110) with the increase in the concentration of Ce and Mn, which is related to d-spacing, i.e. the lattice parameter, $a$, which is determined by the Nelson-Riley function $F(\theta)$ using the equation,

$$F(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$ (1)

The values of the lattice parameters are listed in Table 1. It is observed that the peaks shift to the right (toward the larger angle) for the Ce-doped BaTi$_3$O$_3$ samples and the lattice parameter decreases with the increase in Ce concentration in BaTi$_3$O$_3$, which may be due to the ionic radius of dopant Ce$^{3+}$ (0.102 nm) being smaller than that of Ba$^{2+}$ (0.135 nm) [19]. On the other hand, though the ionic radius of Mn$^{4+}$ (0.064 nm) is smaller than that of Ti$^{4+}$ (0.0745 nm), the peaks shift to the left instead of to the right, and the lattice parameter varies irregularly with the Mn concentration. This may be owing to the tendency of Mn to change its valence, where Mn$^{2+}$ has ionic radii of 0.081 nm (lower spin) and 0.097 nm (higher spin), and Mn$^{3+}$ has 0.072 nm (lower spin) and 0.0785 nm (higher spin) [11]. For the co-doped BaTi$_3$O$_3$, the irregular value of the lattice parameter is also due to this tendency to change the valence of Mn.

The energy-dispersive X-ray (EDX) detector was used for the elemental analysis of the samples, and the relative counts of X-ray versus energy spectrum is obtained. The representative curve as shown in Figure 4 indicates the Ce- and Mn-rich regions, which can be synchronized with the perovskite phase in the Ba$_{1-x}$Ce$_x$Ti$_{1-y}$Mn$_y$O$_3$ with $x = y = 0.02$ sample. The EDX analysis also indicates that there is no impurity element in the sample.

The room temperature $J-V$ characteristic curves of all the samples are shown in Figure 5A–C, which indicate that the current density increases almost linearly with the applied voltage, i.e., the samples show nearly an ohmic nature, which is predicted from the calculated values of the exponent $n$, in the $J \propto V^n$ equation that lies between 0.9 and 1.38 [2]. The values of $n$ of the $J-V$ curves are given in Table 1.

To understand the effect of Ce and Mn doping on the electrical property of the BaTi$_3$O$_3$, the frequency-dependent AC resistivity of the samples was analyzed. Figure 6A shows the variation of resistivity with frequency of the different compositions of BaTi$_3$O$_3$, where it is observed that in the lower-frequency region (up to 100 kHz), resistivity drops sharply as the frequency increases, but at the higher-frequency region, it becomes independent of frequency. Figure 6B shows the variation of resistivity with the concentration of dopants. The resistivity of the samples is observed to decrease in all cases with the concentration of doping. As a consequence of strong dependence of resistivity on the grain size of the BaTi$_3$O$_3$, it can be conjectured that with the increase in grain size, resistivity decreases. The decreases in resistivity with the increase in Ce doping may be due to the better compaction of the samples. Furthermore, a partial exchange between the Ba$^{3+}$ and Ce$^{3+}$ sites may cause the increase in carrier concentration, and therefore, resistivity decreases [2]. Similar results are also observed for the Mn-doped BaTi$_3$O$_3$ and Ce, Mn co-doped BaTi$_3$O$_3$ samples.
It is observed from Figure 7A that at a very low frequency (below 1 kHz), the value of the dielectric constant $\varepsilon_r$ decreases with increasing frequency [2, 20–23], which suggests that the presence of more than one kind of polarization (i.e. interfacial, atomic, dipolar, electronic, etc.) is effective in the samples. However, beyond 1.5 kHz, $\varepsilon_r$ becomes almost constant with frequency. At a higher-frequency region, it may be conjectured that mainly atomic and electronic polarization contributes to $\varepsilon_r$ [24]. Again, the value of $\varepsilon_r$ increases with the increase in the doping concentration in BaTiO$_3$. The result given in Table 1 shows that the addition of Mn causes a slight increase.
in $\varepsilon_r$, and a further increase occurs due to Mn and Ce co-doping. However, BaTiO$_3$ doped with 3 wt% Ce shows the highest $\varepsilon_r$ value. As the lattice parameter decreases with doping and co-doping, there may be an increase in density of the samples [2]. Again, the increase in density increases the dielectric constant [25]. So the increase in the dielectric constant of the doped and co-doped BaTiO$_3$ could be happened due to the increase in the density with doping.

The variation of the dielectric loss $D$ with frequency for the different compositions of the samples is shown in Figure 7B, where the $D$ value drops gradually in the lower-frequency region (up to 4 kHz) and, then, remains almost constant at the higher-frequency region. However, at a higher-frequency range, the value of $D$ decreases slightly with the increase in frequency. In the case of the Ce-doped BaTiO$_3$, the value of $D$ decreases as the doping concentration increases [2]. For the Mn-doped BaTiO$_3$, the $D$ value varies irregularly with the increase in the concentration of the dopant.

### 4 Conclusions

The grains of the Ba$_{1-x}$Ce$_x$Ti$_{1-y}$Mn$_y$O$_3$ samples are observed to be of irregular shape. Although Ce doping has a significant effect on the increase in grain size of the ceramics, no such sharp increase in grain size is observed for Mn doping. The XRD pattern confirmed the single-phase structure of the samples having a very small amount of impurity phases, which reduces due to the addition of Ce and Mn in BaTiO$_3$. All the samples show nearly an ohmic nature with very low conductivity. The AC resistivity, dielectric constant, and dielectric loss of the samples decrease in the low-frequency region, but the AC resistivity and the dielectric constant became nearly constant above 100 kHz and above 1 kHz, respectively. The value of the resistivity decreases and the dielectric constant increases with Ce and Mn concentration. Besides, the dielectric loss is observed to decrease with the increase in the concentration of the Ce dopant, but the variation becomes irregular when Mn is doped. BaTiO$_3$ doped with Mn showed an improved property than that of pure BaTiO$_3$, but further improvement can be achieved by co-doping with Ce. Although a better result can be obtained from the Ce-doped BaTiO$_3$, to reduce the production cost, it would be convenient to co-dope BaTiO$_3$ with Ce and Mn.

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