Dielectric and microstructural properties of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ ceramics

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Abstract. $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ ceramics were investigated regarding their dielectric and microstructure properties via conventional solid state reaction method. The phase pure samples were obtained when heated at 1400˚C for overnight. The effect of Er^{3+} doped into $BaTiO_3$ on dielectric properties and microstructural properties was investigated for composition of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$. The analysis was made by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Impedance Analyzer. The XRD patterns of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ are phase pure and identical with tetragonal perovskite structure with space group of P4mm. The lattice parameters and unit cell volume of $BaTiO_3$ increased by doping with Erbium as the crystallite size decreased. Measurements of dielectric properties were carried out as a function of temperature up to 200˚C at different frequencies. $Ba_{0.9925}Er_{0.0075}TiO_3$ exhibit the high value of dielectric constant (ε=6179) at Curie temperature (T_C) of 120˚C. SEM analysis of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ ceramics showed that the grain sizes of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ were ranged from 3.3μm-7.8μm and 2.2μm-4.7μm respectively.

1 Introduction

The Barium titanate ($BaTiO_3$) – based ferroelectric ceramics have gained importance in electronic industry as they have high dielectric constant and offer wide range of applications such as capacitors, sensors, actuators, power transmission devices, memory devices and high energy storage devices [1-2]. $BaTiO_3$ has a perovskite structure and due to this perovskite structure, $BaTiO_3$ has intrinsic capability to host different dopant ions with different sizes. The influence of dopant ion depends on the substitutional site (Ba^{2+} or Ti^{4+}) as well as on the defects itself. The ionic radius of the dopant ion is essential for the determination of the substitutional site of host material. The ions with small ionic radii such as La^{3+} and Ce^{3+}will substitute into A- site whereas the ions with bigger ionic radii such as Lu^{3+} and Yb^{3+} possibly substitute at B site of $BaTiO_3$ structure. The ions that have amphoteric behaviour such as Y^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+} can occupy both cation lattice site in the $BaTiO_3$ structure [3-4]. The influence of the dopant incorporation into $BaTiO_3$ as well as the influence of some transition metal and large rare earth ions in the structural and electrical properties of $BaTiO_3$ ceramics has been extensively investigated. Among them, Erbium (Er^{3+}) has been widely used due to its great technological interest. It has been previously reported by Leyet et. al. [5] that with the Erbium cation incorporation into $BaTiO_3$ crystalline lattice according to the formula $Ba_{1-x}Er_xTiO_3$, increase in dielectric constant is observed. This suggests that the incorporation of Er^{3+} into $BaTiO_3$ crystalline lattice can be greatly improve the dielectric properties of $BaTiO_3$.The aim of this work is to investigate the structural and electrical properties of Er doped $BaTiO_3$ as a function of the Er^{3+} concentration as well as to correlate the structure properties of pure $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$.

2 Experimental

$BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ compositions were prepared via conventional solid state reaction method. The chemicals used were high purity of $BaCO_3$ (99.99% Pure, Sigma-Aldrich), USA), TiO_2 (99.99%, Sigma-Aldrich) and Er_2O_3 (99%, Sigma-Aldrich) powders. $BaCO_3$, TiO_2 and Er_2O_3 were weighed using **A**&D Weighing HR250AZ pharma balance. Powder samples were mixed and ground using pestle and mortar. Samples were ground for half an hour by hand using acetone as the medium for mixing. Samples were then pressed into pellets shape by using uniaxial press with 1 tonne pressured. Pellets were then heated in air at high temperature between 1000°C and 1400°C at 5°C/min for overnight. The crystal structures of the samples were confirmed by using X-ray Diffraction (Bruker,D2-Phaser) with Cu Kα radiation (λ = 1.5406). Samples

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were measured in range of 2θ = 20° - 80° using step size of 0.02. The sintering temperature for electrical measurement was 1300°C for 3 hours with heating and cooling rate of about 5°C/min in air. For electrical measurements, the surfaces of sintered pellets were painted with silver conductive paint. The electrical characterization is measured using Impedance Analyser (Hioki IM3570) from room temperature to 200˚C at 1kHz, 10 kHz and 100 kHz. The microstructure was studied by using Scanning Electron Microscopy (SEM). The SEM micrographs were obtained using a JEOL JSM-6460LA SEM. The grains size distribution was measured using SEM image analysis software, Smile View.

3 Results and Discussions

3.1 XRD Analysis

Fig. 1 shows the X-ray Diffraction (XRD) patterns of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ samples heated at 1400˚C for overnight. The XRD patterns show similar XRD pattern with an early reported $BaTiO_3$ tetragonal perovskite structure [6, 7]. The XRD patterns are the same and show the single phase tetragonal perovskite structure with space group of P4mm. The lattice parameters and unit cell volume for the sample $BaTiO_3$ composition sintered at 1400°C were a = 3.9918 Å and c = 4.0338 Å and unit cell volume, V = 64.28 Å^3. The lattice parameters and unit cell volume for the sample $Ba_{0.9925}Er_{0.0075}TiO_3$ composition sintered at 1400°C were a = 3.9940 Å and c = 4.0362 Å and unit cell volume, V = 64.38 Å^3. Table 1 shows the structure parameters of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ obtained. An increase in lattice parameters of $BaTiO_3$ as doped with Er can be observed. The average crystallite size values of pure $BaTiO_3$ and Erbium doped $BaTiO_3$ ceramics, revealing there is a decrease in the size suggesting the effect of dopant on crystallite size of $BaTiO_3$. The crystallite sizes were evaluated through the Scherrer's equation. It is commonly determined by measuring the Bragg's peak width at the half maximum intensity and by using the Scherrer's formula (Eq. 1), where d is the crystalline size, λ is the wavelength of the x-ray, ß is the peak width at the half maximum intensity and theta is the Bragg's angle [7].

$$d = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Table 1. Structural parameters of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ prepared samples and their calculated crystallite sizes.

Sample	*a (Å)*	*c (Å)*	*V(cm^3)*	*Crystallite size (Å)*
$BaTiO_3$	3.9918(3)	4.0338(5)	64.28(2)	1068.44
$Ba_{0.9925}Er_{0.0075}TiO_3$	3.9940(3)	4.0362(5)	64.38(1)	931

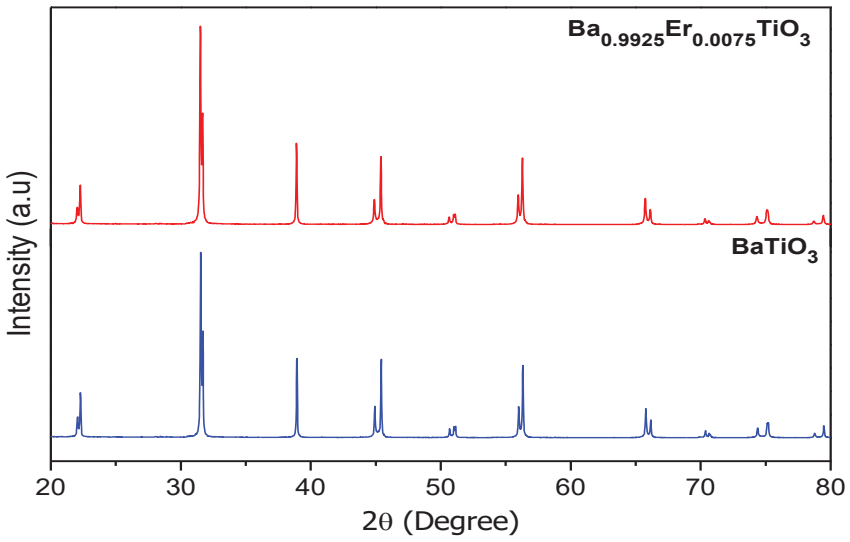

Fig. 1. XRD pattern of $BaTiO_3$and $Ba_{0.9925}Er_{0.0075}TiO_3$ heated at 1400˚C

3.2 Electrical Analysis

The dielectric behavior and dielectric loss as a function of temperature for the sintered pellets of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ at 1 kHz is shown in Fig. 2. It can be observed that by doping, the permittivity increase from 5194 to 6502 for $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$. The Curie temperature, T_C increased by doping which is from 110˚C to 120˚C for $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ respectively. Increase in T_C may be due to the misfit between the grain core and the grain shell give rise to stresses and shift the Curie point to higher temperature

as suggested by Hwang et. al [8]. Some of rare earth doping that increase the T_C are Yb doped $BaTiO_3$ and Lu doped $BaTiO_3$ which is quite similar to the current Er doped $BaTiO_3$ system. Based on Fig. 2, an increase in dielectric constant from 5194 to 6502 for $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ can be observed at 1 kHz. The increase in dielectric constant can be due to the modifications in the grain size, resulting from the incorporation of the erbium in the $BaTiO_3$ structure [5].

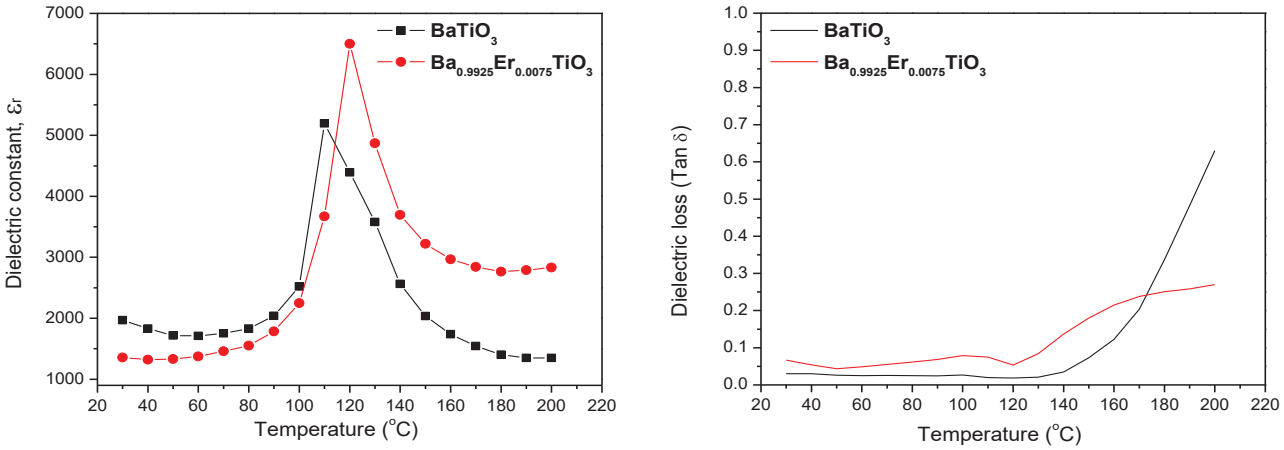

Fig. 2. Dielectric constant and dielectric loss of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ at 1 kHz

As for the dielectric loss, it can be seen that the dielectric loss of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ were less than 0.1 at temperature below 120˚C. Much higher dielectric loss which is more than 0.1 observed at higher temperature above 120˚C up to 200˚C. Table 2 summarizes the dielectric constant values and T_C of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ at different frequencies. The dielectric constant values are decreased as the frequency increased.

Table 2. Dielectric constant and T_C of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ at different frequencies.

Sample	Dielectric constant	Curie temperatre,T_C	Frequency
$BaTiO_3$	5194	110˚C	1kHz
	5072		10kHz
	4880		100kHz
$Ba_{0.9925}Er_{0.0075}TiO_3$	6502	120˚C	1kHz
	6179		10kHz
	5891		100kHz

$Ba_{0.9925}Er_{0.0075}TiO_3$ shows the highest dielectric constant at 1 kHz which increased by almost 1000 as compared to the $BaTiO_3$. The T_C of $Ba_{0.9925}Er_{0.0075}TiO_3$ increased by 10˚C from T_C of $BaTiO_3$. However, as the frequency increased, the dielectric constant values decreased. The decreasing dielectric constant values across the frequencies may be due to space charge polarization as reported by Ganguly et al. [9]. Fig. 3(a) shows the variation of capacitance value for undoped $BaTiO_3$ and Er doped $BaTiO_3$ at x=0.0075. The capacitance values increases from about ~$3x10^{-9}$ Fcm^{-1} to ~$4x10^{-9}$ Fcm^{-1} by doping Er into $BaTiO_3$. These results are consistent with the results of dielectric constant. Fig. 3(b) shows the conductivity values of $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ at specific temperatures from 30˚C to 200˚C. The conductivity was between ~10^{-7} Scm^{-1} and ~10^{-6} Scm^{-1}.The conductivity of $BaTiO_3$ shows the trend for insulator behavior which increased from room temperature to T_C and decreased after T_C. For $Ba_{0.9925}Er_{0.0075}TiO_3$, the conductivity of samples shows

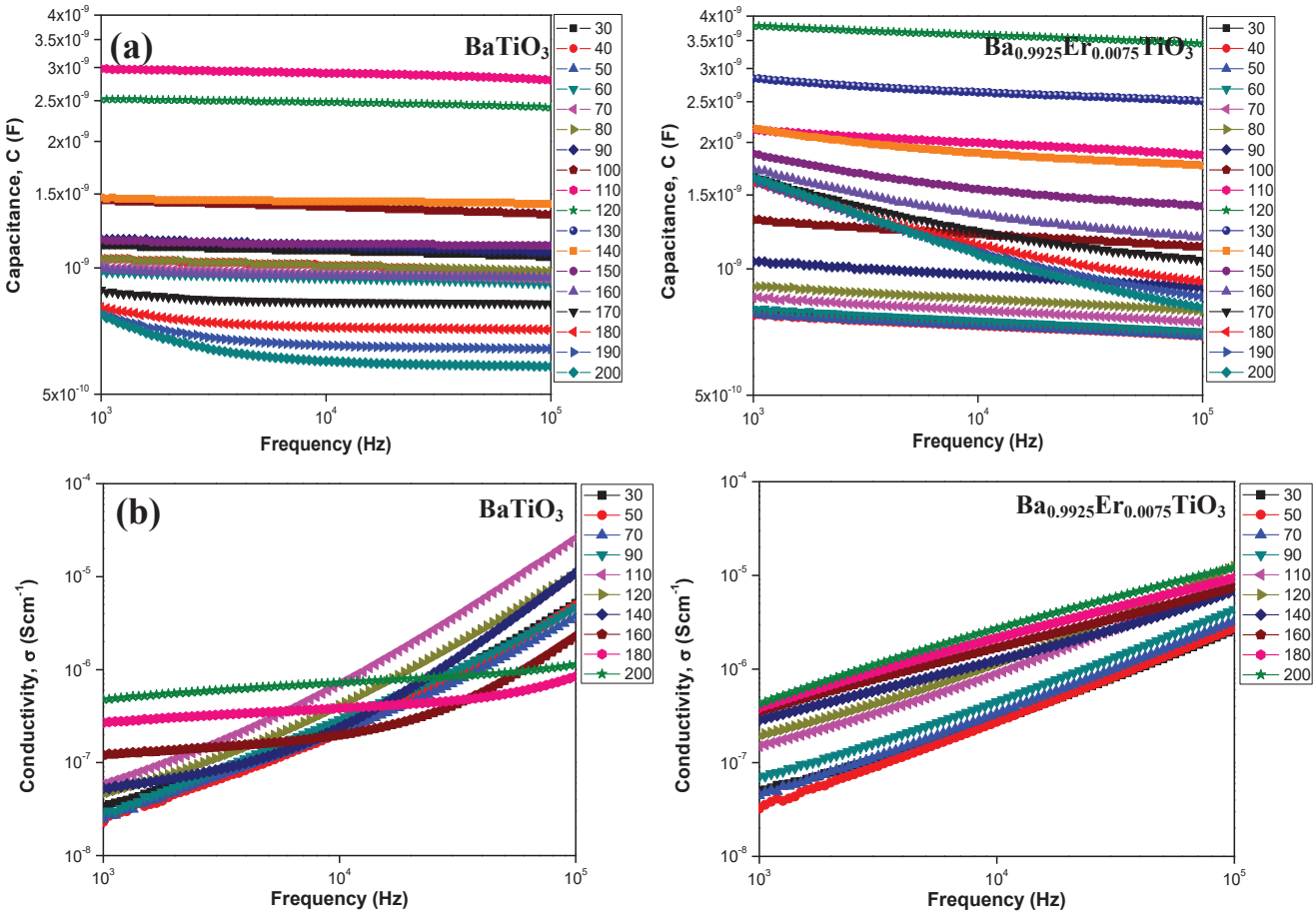

Fig. 3. a) Capacitance and b) conductivity of $BaTiO_3$ and $Ba_{1-0.9925}Er_{0.0075}TiO_3$ as a function of frequencies at different temperature

the typical ceramic behavior which increased as the temperature increased.

3.3 Microstructural Analysis

Fig. 4 shows that the surface morphology of sintered $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ by using SEM. The relation between dielectric constant and the grain size of sintered $BaTiO_3$ and $Ba_{0.9925}Er_{0.0075}TiO_3$ were observed. These micrographs were captured by 1000x magnification using Secondary Electron (SE) mode.

From Fig. 4(a) and 4(b), the irregular shape of grains can be seen for both samples. However, there is difference in the grain size as shown in grain size distribution graph in Fig. 5(a) and 5(b). The grain size of $BaTiO_3$ was in between 3.3μm-7.8μm and the grain size for $Ba_{0.9925}Er_{0.0075}TiO_3$ was ranged from 2.2μm-4.7μm. The grain size of $Ba_{0.9925}Er_{0.0075}TiO_3$ is much smaller as compared to $BaTiO_3$. Therefore, the dielectric constant of $Ba_{0.9925}Er_{0.0075}TiO_3$ sample is much higher than $BaTiO_3$ samples.

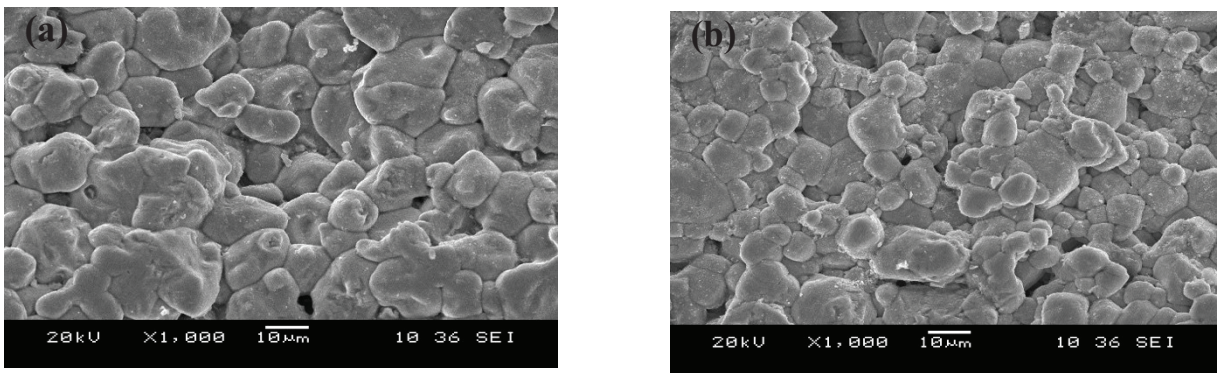

Fig. 4. Scanning electron micrographs of sintered (a) $BaTiO_3$ and (b) $Ba_{1-0.9925}Er_{0.0075}TiO_3$ at 1000x magnification

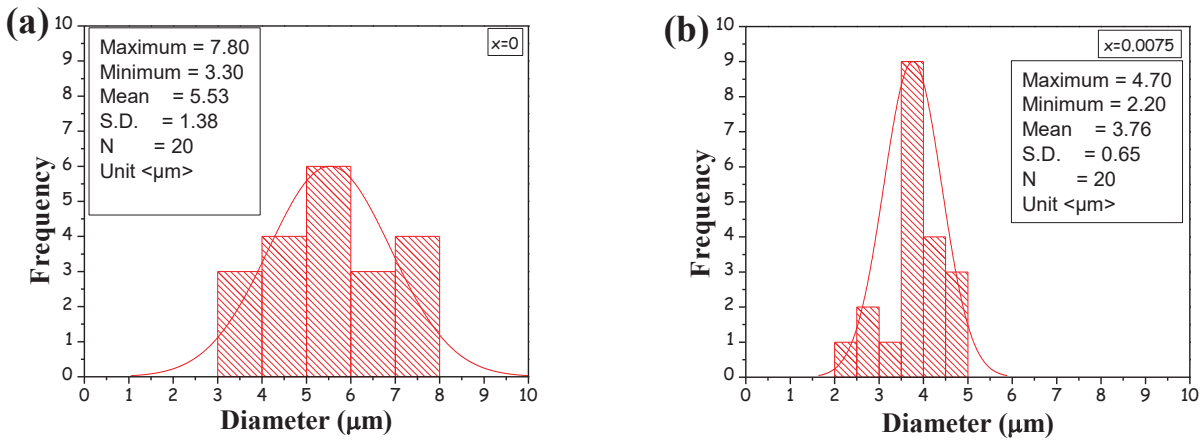

Fig. 5. Grain size distribution of sintered (a) $BaTiO_3$ and (b) $Ba_{1-0.9925}Er_{0.0075}TiO_3$ at 1000x magnification

4 Conclusions

Doping study using Erbium doped $BaTiO_3$ was studied with the effect of small amount of Er to the A-site of $BaTiO_3$. The dielectric behaviour of $BaTiO_3$ improved by doping. The highest dielectric constant observed at Er doped $BaTiO_3$ with dielectric constant maximum at T_C about 120˚C which is 6502. As for dielectric loss, the value is lower than 0.1. Besides, the capacitance and conductivity also improved significantly. The capacitance increased from ~$3x10^{-9}$ Fcm^{-1} to ~4 x 10^{-9} Fcm^{-1}. The conductivity was between ~10^{-7} Scm^{-1} and ~10^{-6} Scm^{-1}. The effects of Erbium doping on the microstructural properties were verified as the grain size decreased as Er doped into $BaTiO_3$. The grain size of $BaTiO_3$ was in between 3.3 μm - 7.8 μm which is larger as compared to the grain size for $Ba_{0.9925}Er_{0.0075}TiO_3$ ranged from 2.2 μm - 4.7 μm. Finally, it can be concluded that by doping Er into $BaTiO_3$, the dielectric properties were improved and can be correlated with microstructure properties.

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