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Comparative studies of Cerium and Zirconium doped Barium Titanate

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Abstract: Comparative investigations of microstructure and dielectric properties of BaTiO_3 ceramics doped with different concentration of CeO_2 and ZrO_2 have been studied. BaTiO_3 samples were prepared using conventional method of solid state sintering at 1250°C for four hours. Distinct microstructure was observed with pure and doped BaTiO_3 . The highest value of dielectric permittivity and the lowest value of loss tangent was found for CeO_2 with $x=0.1$ mole percent. In all investigated samples dielectric constant assumes initially large value at low frequencies ($\approx 75\text{KHz}$) and attains constant value at frequency $\approx 1\text{MHz}$.

Keywords: BaTiO_3 , ceramic, dielectric properties, grain size, resistivity.

I. Introduction

Ferroelectric BaTiO_3 is most commonly used as capacitors, thermistors, varistors and energy converting systems depending on suitable additives. The permittivity of ferroelectric perovskite shows marked change with temperature near transition temperature and frequency (relaxation point). BaTiO_3 powder is usually mixed with various types of additives in order to obtain better performance and a good control over grain size and electrical characteristics of ceramics. It has been found that the dielectric properties of polycrystalline BaTiO_3 depend to a great extent, on the grain growth during sintering, on additive type and concentration^{[1]-[3]}.

For the application of doped BaTiO_3 ceramics as a capacitor, material apart from good density, a high dielectric constant and low loss factor have to be achieved. The main factors that must be taken into account during the processing of ceramics are the homogenization of BaTiO_3 powder with a suitable doping concentration, the sintering temperature and the length of time. For capacitor type application, the primary requirements are the high permittivity characteristics and a small temperature variation of permittivity over a wide temperature region. Barium titanate is usually doped with variety of additives such as Bi_2O_3 , CeO_2 , ZrO_2 , Nb_2O_5 , Dy_2O_3 and other oxides, which enhance either sintering rate or densification degree^{[4],[5]} to achieve temperature stable dielectrics.

Among the dopants that are used to modify the dielectric and semi conducting properties of BaTiO_3 , Zirconium and Cerium are the most useful donor dependent that can be incorporated in Ti^{+2} sites or Ba^{+2} sites. Depending on their concentration (Zr or Ce), in BaTiO_3 may exhibit semiconducting or insulating properties.

Influence of CeO_2 on electrical and semiconducting properties of BaTiO_3 has been widely investigated^{[8],[9]}. An interesting aspect of CeO_2 is the special chemistry of Ce^{+4} which can readily reduce itself to Ce^{+3} . This property is the basis of several technological applications of CeO^{+2} , such as catalytic supports (for automatic exhaust) and high temperature electrodes. Among the dopant elements, ZrO_2 and CeO_2 are used to modify the dielectric and semi conducting properties of BaTiO_3 , because of their electric and catalytic properties, which are related to oxygen stoichiometry.

Studies on the effect of Zr addition to BaTiO_3 show that Zr addition shift the curie point and depress the dielectric peak. Zr^{+4} can substitute Ti^{+4} ions as isovalent doping. Addition of Zirconia particles into Barium titanate can form a core shell structure^[11]. The desired temperature stability in dielectric properties is achieved by the formation of core-shell grain. The aim of this paper is to compare the microstructures and dielectric measurements of Barium Titanate doped with Zr and Ce as a function of ac electric field.

II. Material and Methods

A. Sample preparation

The doped specimens used for this investigation were prepared by conventional solid state reaction technique^[8]. Analytical grade of BaO , TiO_2 , ZrO_2 and CeO_2 were used to make ceramic mixed crystals of $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ and $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$. The disks of 6 mm diameter and approximately of 2 mm thickness were prepared and sintered at 1250°C for four hours in a furnace. Silver paste was used on both sides of the disks for good contact.

B. Measurements

Furnace (type-ROS 3/20 FNR 7601905 Hochest, temperature 1500°C , Germany) was used for sintering the samples. In this experiment, Agilent 4216 precision LCR meter was used for measuring capacitance(C), resistance(R) and dissipation factor (D) in the frequency range from 75 KHz to 32 MHz.

The microstructure and grain size of the as-sintered ceramic samples were determined by a Hitachi S-3400 N variable pressure scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) attachment. Microstructure evaluations were made from as-sintered surface of the samples. The evaluation of grain size and concentration of the elementary particles were monitored by SEM-image and EDS spectra consequently.

III. Results and discussions

A. Microstructural characteristics

All the samples sintered at 1250°C for four hours were studied by scanning electron microscope. SEM study of the samples revealed that the sintering took place without grain growth.

Figure 1: SEM images of (a) Pure BaTiO₃, (b) x=0.1 ZrBT, (c) x=0.2 ZrBT, (d) x=0.3 ZrBT, (e) x=0.4 ZrBT (f) x=0.1 CeBT and (g) x=0.2 CeBT (h) x=0.3 CeBT (i) 0.4 CeBT

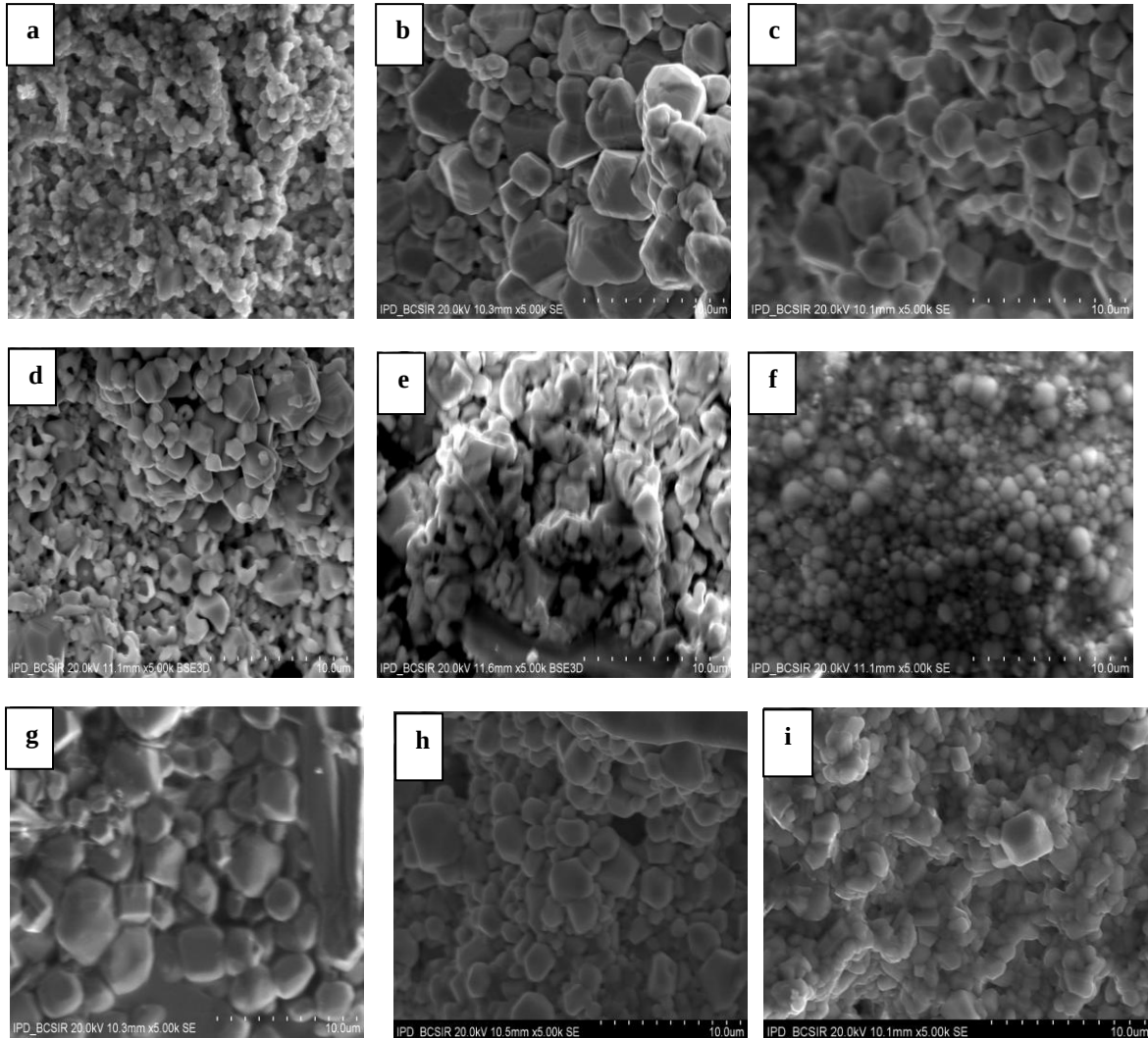


Fig.1 shows the microstructure of pure BaTiO₃ ceramics which exhibits normal grain growth, a fairly uniform microstructure and homogeneous distribution of BaO and TiO₂. The microstructure of BT ceramic doped with ZrO₂ and CeO₂ at different concentrations exhibit homogeneous grain size. Addition of different concentration of Zr and Ce with pure BT ceramics has influence on dielectric property and microstructure of the as-sintered sample. Figures show the significant change in grain size with small addition of doping element. Average grain sizes of the samples are calculated from the microstructure of the surface taken from Scanning Electron Microscope. Five or six determinations of diameter are made at random and the average is computed from the measurements.

Fig. 1(a) exhibits normal grain growth of pure BaTiO₃ and shows a fairly uniform microstructure and homogeneous distribution of BaO and TiO₂. It is observed that the average grain size is 1.024 μm in case of pure BaTiO₃. Uniformity of microstructure is revealed from EDS analysis. The microstructures of Ce doped BaTiO₃ with different concentrations show fairly uniform distribution of the constituent elements with different grain size. Micrograph shows that there are coarse grains as well as small grain. Some Ce and Zr rich regions

were detected in microstructure from point shooting analysis of EDS spectra. The additive rich phases are formed in local regions due to insufficient homogenisation of starting powders. The presence of chemically inhomogeneous system in Ce or Zr doped BaTiO₃ samples may be the cause of the decrease of dielectric constant.

Table I: The grain size of Ce and Zr doped BT

Sample No.	x	Composition of the sample	Average grain size of Ce doped BT(μm)	Composition of the sample	Average grain size of Zr doped BT(μm)
1	0.0	BaTiO ₃	1.024	BaTiO ₃	1.024
2	0.1	Ba _{0.9} Ce _{0.1} TiO ₃	1.69	Ba(Ti _{0.9} Zr _{0.1})O ₃	4.158
3	0.2	Ba _{0.8} Ce _{0.2} TiO ₃	1.31	Ba(Ti _{0.8} Zr _{0.2})O ₃	2.113
4	0.3	Ba _{0.7} Ce _{0.3} TiO ₃	1.42	Ba(Ti _{0.7} Zr _{0.3})O ₃	1.538

Table 1 shows the grain size of Ce and Zr doped BT. The grain size of Ce doped BT is smaller than the grain size of Zr doped BT.

Figure 2(a): EDS spectra of pure BaTiO₃

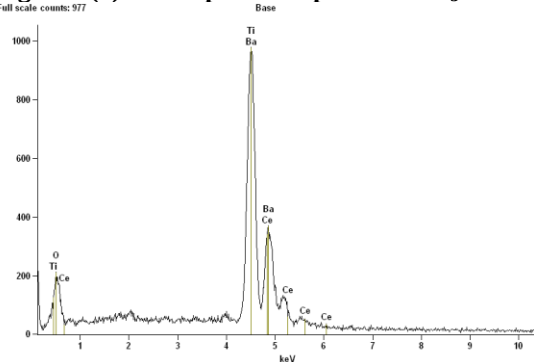


Figure 2(b): EDS spectra of Ce-doped BaTiO₃

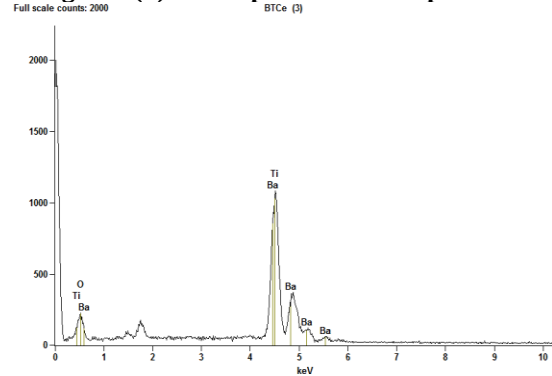
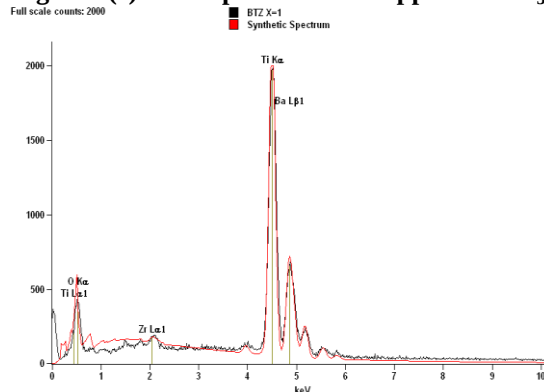


Figure 2(c): EDS spectra of Zr-doped BaTiO₃



Fig(2a), Fig(2b), Fig(2c) shows the EDS spectra of pure and Ce and Zr doped BaTiO₃ respectively. EDS spectra confirms the presence of elemental compositions.

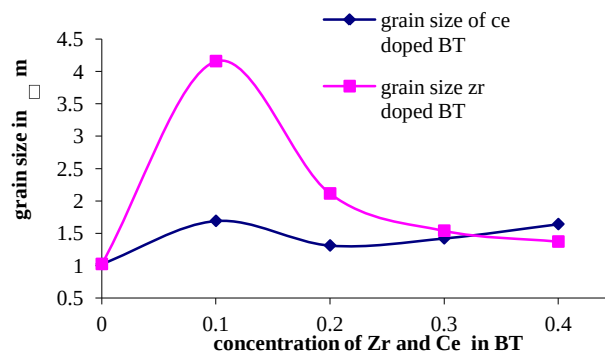


Figure 3: Change of grain size with concentration of Ce and Zr doping

Fig.3 Shows the Change of grain size with percentage of doping element. The change in grain size with percentage composition of Ce and Zr shows the similar trend. As the concentration increases grain size increases upto x=0.1 and then decreases in both cases of doping.

IV. Dielectric measurements

The effect of microstructure of dielectric properties of pure and doped BaTiO_3 at high frequency was studied experimentally. The observed microstructural features together with the type of additives have a direct influence on the dielectric properties of doped BT. The dielectric constant and loss factor of the samples were measured as a function of frequency^{[10], [11]}. The effect of Zr and Ce in pure BT are shown in Fig.4 and Fig.5. Fig.4 shows that the presence of doping element such as Ce and Zr increases dielectric constant compared to pure BaTiO_3 . The higher value of dielectric constant and low loss in low frequency is found for the sample Ce doped BT than Zr doped BT. In Ce doped BT, small addition of CeO_2 ($x=0.1$) increases grain size as well as dielectric constant compared to pure BT. It is observed that $\tan\delta$ as well as dielectric constant decreases with the increase of Ce content (>0.1). Similar behavior is observed in the case of Zr doped BT.

Figure 4: Frequency Vs Dielectric Constant of Ce and Zr doped BaTiO_3

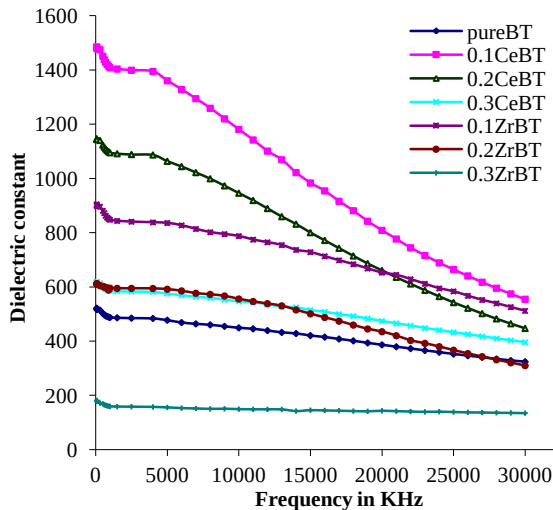
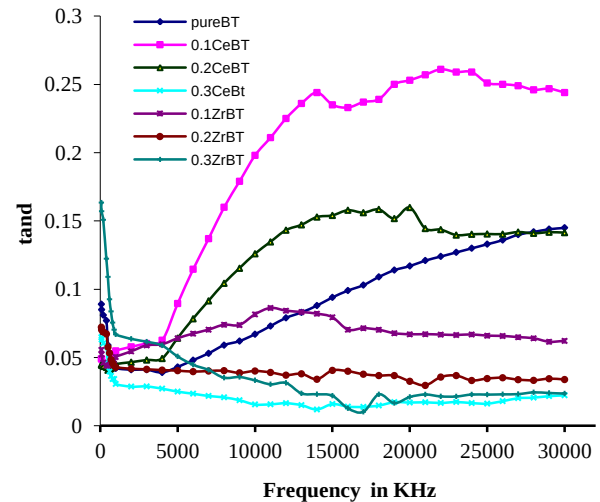


Figure 5: Frequency Vs. $\tan\delta$ of Ce and Zr doped BaTiO_3



Ac field dependence on loss factor is illustrated for samples doped with Zr and Ce in Fig.5. In Ce doped BT samples the relaxation occurs at 1MHz for all the samples except in case of $x=0.3$ and Zr doped BT sample shows no significant relaxation in our present experiment.

VI. Frequency response resistivity

The resistivity at room temperature in the frequency range 75KHz-30MHz shows the resistivity ρ which falls to lower value than at higher frequency region. With the increase of CeO_2 and ZrO_2 , the resistivity of the samples show same characteristics up to $x=0.2$ for all samples but the value of the resistivity as well as dielectric constant increase for further addition of Zr and Ce in BT in the present experiment. Resistivity of the samples also depends on the grain size. It is evident that Ce doped BaTiO_3 shows high resistivity than Zr doped BT as shown in Fig.6 and Fig.7 which corresponds to high dielectric constant subsequently.

Figure 6: Value of x in $\text{Ba}_x\text{Ce}_{1-x}\text{TiO}_3$

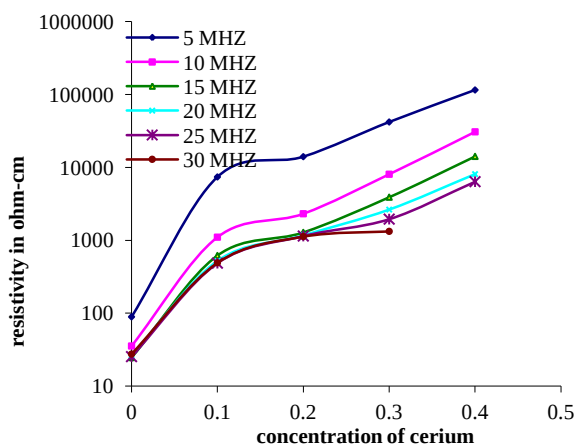
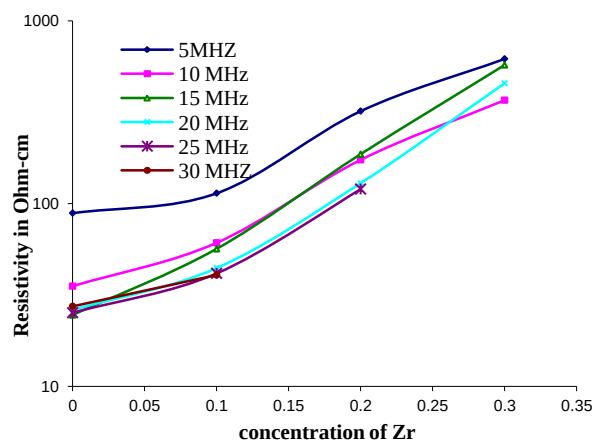


Figure 7: Value of x in $\text{BaZr}_{1-x}\text{TiO}_{3x}$



VII. Conclusions

Comparative investigation of microstructure and dielectric properties of ceramics doped with Ce and Zr have been studied. Different microstructure regions were observed in the samples. The highest value of permittivity

was observed in the case of $x=0.1$ Ce doped BaTiO_3 at frequency 75Hz which is characterized by fairly uniform microstructure with a homogenous distribution of additives. Dielectric constant is influenced not only by doping elements but also by concentration of doping element and grain size. A high dielectric constant (1485) was attained for the doping element CeO_2 for $x=0.1$ at frequency 75KHz with low dissipation factor. The relaxation peaks are mainly due to the diffusion of oxygen vacancies induced by the acceptor impurities in an electrical field induced by variation of polarization of the material under electrical excitation.

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