Optimum Amount of Zirconium in Barium Titanate for Better Electric and Dielectric Properties

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Abstract: *Barium zirconium titanate ceramics Ba $(Zr_xTi_{(1-x)})$ O_3(x=0.,0.05,0.10,0.15 and 0.2) were prepared by a sol-gel method. Perovskite-like single-phase compounds were confirmed from X-ray diffraction data. Morphological analysis of calcined samples done by scanning electron microscopy shows that the addition of zirconium ions affects the size of the grain and remarkably changes the grain morphology. The effect of zirconium addition to barium titanate on its dielectric properties were analysed. Increasing zirconium content in the BaTiO₃-based compositions caused an increase in the width of Curie temperature (Tc) and an increase in the permittivity.*

Keywords: Barium Zirconium Titanate, Dielectric Properties, Curie Temperature, Dissipation Factor

1. Introduction

Barium titanate ceramics are of great interest owing to their ferroelectric and dielectric properties [1-2]. However, barium titanate in its pure form shows a relatively sharp Tc~120°C this limits its use as a high-power transducer and as a piezoelectric material [3]. It is due to the multiple ferroelectric phase transitions and the significant temperature dependence of piezoelectric properties of it. Another disadvantage of pure barium titanate is its high temperature coefficient of capacitance [4], which is a consequence of transition from tetragonal to cubic phase. Barium titanate powder is usually mixed with various types of additives in order to obtain better performances and a good control over grain size and electrical characteristics. Isovalent dopants, such as strontium and zirconium [5-7], are often employed to shift the Curie point. The Zr^{4+} ion is chemically more stable than the Ti^{4+} and a partial substitution of Ti^{4+} with Zr^{4+}, forms the solid solution $BaZr_xTi_{1-x}O_3$, with an associated increase in the lattice parameter and consequent change in the crystal structure, phase transition temperatures and the dielectric properties compared to pure $BaTiO_3$. Many researchers studied reported the substitution of zirconium for titanium in $BaTiO_3$ [8-10]

It's clear from the literature that, zirconium doped barium titanate material exhibits several interesting features in its dielectric behaviour. The ferroelectric phase transition as well as dielectric properties of zirconium doped barium titanate ceramics is strongly influenced by the amount of zirconium in the matrix. In the present study, zirconium doped $BaTiO_3$ powders were prepared by doping different wt. % zirconium using sol-gel technique to optimise the zirconium content for better dielectric properties.

2. Experiment

Zirconium doped barium titanate was synthesized by the sol-gel method. Detailed procedure for preparation $BaTiO_3$ ceramic powders and the pellet preparation has been described in our previous paper [11]. In addition to the above-mentioned procedure, here zirconium was doped with barium titanate by doping different wt% of zirconium (IV) isopropoxide isopropanol into titanium (IV) isopropoxide as *Ba $(Zr_xTi_{(1-x)})$ O_3(x=0.,0.05,0.10,0.15 and 0.2),* during the reaction.

Table 1: Amount of Zirconium(IV) isopropoxide isopropanol taken for doping different wt% of zirconium

Wt % of zirconium	Zirconium(IV) isopropoxide isopropanol	Titanium(IV) isopropoxide
0	-	13.528 ml
0.05	0.59745 g	8.3229 ml
0.1	1.19497 g	7.8849 ml
0.15	1.79246 g	7.4468 ml
0.20	2.3899 g	7.0088 ml

3. Results and Discussions

3.1 *DTA-TG*

Thermal analyses (TGA, DTA,) of the pure $BaTiO_3$ powder precursor and 0.2 wt% zirconium added powder precursor prepared by sol gel are shown in figure1 (a-b). The TG and DTG of the gel were carried out at a heating rate of 20°C/min up to 840 °C, in air. The weight loss of samples

is shown. The major weight loss occurs upto 200^0C, corresponding to the volatilisation of absorbed water on the grain surface, evaporation of isopropanol, acetic acid and methoxy ethanol respectively. Up to 800^0C transition from $BaCO_3$ and TiO_2 to $BaTiO_3$ occurs which is shown by disturbances in graph. So, we choose 900^0C as the calcination temperature. Calcination temperature was also confirmed in our previous paper [12] by calcining different temperature.
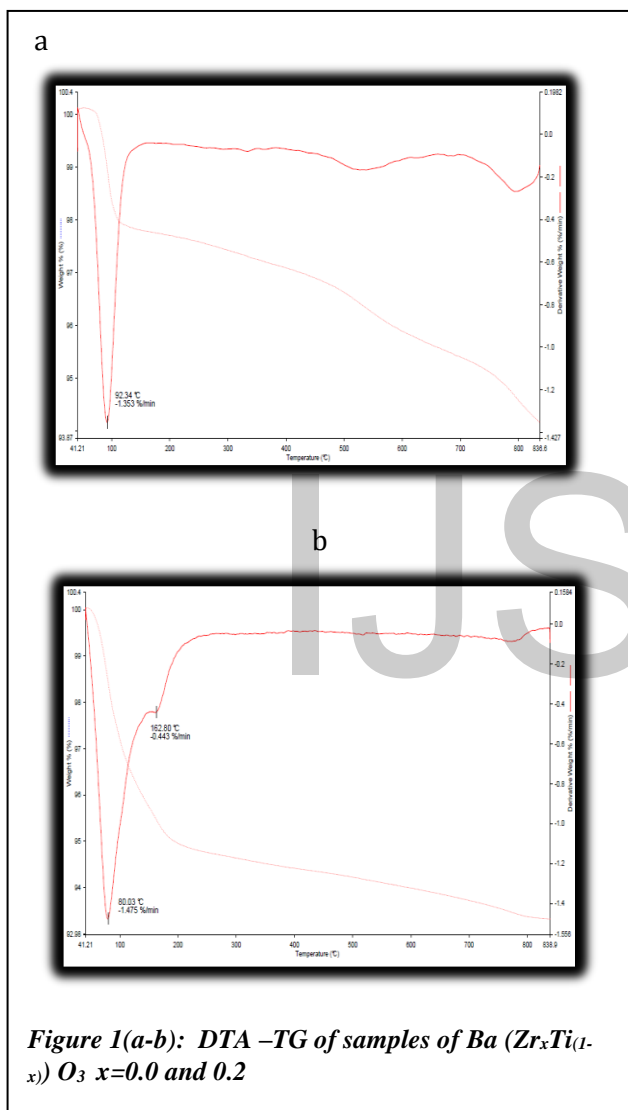

Figure 1(a-b): DTA –TG of samples of Ba (Zr$_x$Ti$_{(1-x)}$) O$_3$ x=0.0 and 0.2

3.2 X-Ray Analysis:

Phase analysis of the samples after calcination was confirmed from X-ray diffraction patterns as shown in figure 2.It also confirmed the mono-phase character of samples when compared to the chemical composition of the assumed standards. Chemical compounds with the perovskite structure were formed in the system $BaZr_xTi_{1x}O_3$ with the zirconium substitution up to $x\leq0.2$. XRD pattern of *Ba (Zr$_x$Ti$_{(1-x)}$)O$_3$ (x=0.05,0.10,0.15 and 0.2)*, suggesting there is not much change in peak intensity as compared to pure $BaTiO_3$. It can be seen that with Zr substitution in

$BaTiO_3$, the 2θ peaks shifted towards lower angle side, indicating increase in the value of lattice parameter as suggested by Sandeep Mahajan et al [7]. The particle size of $BaZr_xTi_{1-x}O_3$ have been determined using the famous Scherrer equation $t=0.9\lambda/(\beta\cos\theta)$ and shown in table 2.
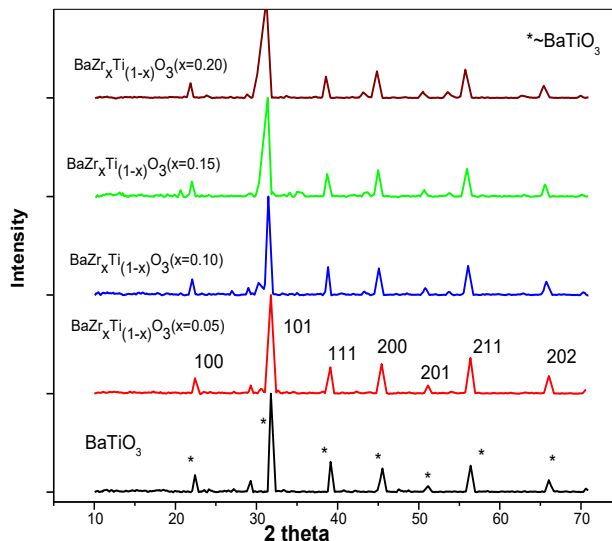

Figure2: XRD patterns of Ba (Zr$_x$Ti$_{(1-x)}$) O$_3$ (x=0.05,0.10,0.15 and 0.2) after calcination at 900^oC

Table 2: The variation of particle size with respect to the amount of zirconium

Ba(Ti$_x$Zr$_{1-x}$)O$_3$ powder (in %)	Crystalline size (nm)
0	0.44050
0.5	0.4946
0.10	0.4435
0.15	0.5071
0.20	0.5709

3. 3 SEM Analysis

The SEM images of the $BaZr_xTi_{1-x}$ O$_3$ samples before and after calcination at 900°c for 4 hours for various compositions (x=0,0.05, 0.10,0.15and 0.2) at 1500x magnification are shown in figure 3(a-e). All the samples exhibited dense grain structures. The samples before calcination has almost same grain size. However, after sintering SEM revealed the presence of spherical and rod-shaped structures. All calcined samples are densely packed with larger grain size and the fracture reveals a brittle nature. Pores have an irregular shape without carvings and narrowing. Grain boundaries are also seen, and a glassy phase is hard to find. In the photographs individual grains and growth terraces are seen and grain size increases as the zirconium content increases and the zirconium content above 0.15 wt % the shape and texture of the grains are changed.
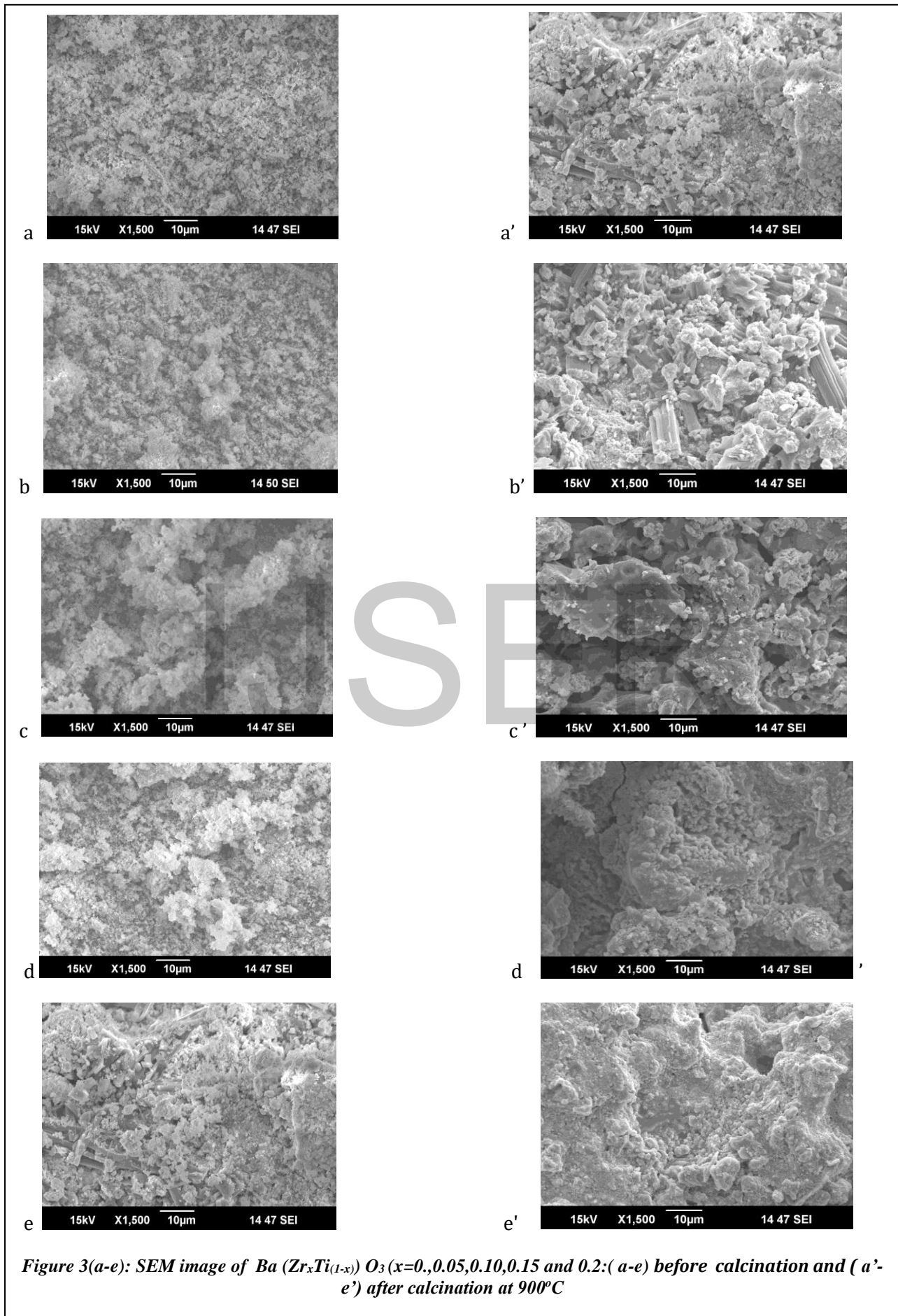
Figure 3(a-e): SEM image of Ba (Zr$_x$Ti$_{(1-x)}$) O$_3$ (x=0.,0.05,0.10,0.15 and 0.2:(a-e) before calcination and (a'-e') after calcination at 900ºC

3.4 Dielectric behaviour

The variation of Curie temperature and the dielectric constant with respect to the various proportions of zirconium in the matrix was studied and shown in the figure 4.From the figure it is clear that the undoped samples have curves similar to the standard dielectric curve of $BaTiO_3$ i.e. dielectric constant value gradually increases with temperature, and then suddenly reaches a peak value at Curie temperature and then decreases. The Curie temperature and corresponding dielectric constants are tabulated in table 3. It is clear from the table 3 that the amount of zirconium increases broadening and flattening of the maximum of $\varepsilon(T)$ as well as shifts the Curie temperatureTc. It's interesting to note that as the zirconium content became 0.05 wt.% dielectric value has increased 67% from that of undoped $BaTiO_3$ and the transition point has broadened to 5^oC. As the zirconium content increases from 0.05 to 0.1 broadening of transition point increases to 40^0C but the dielectric value reduced which may be due to decrease in particle size shown in table 2. By increasing the
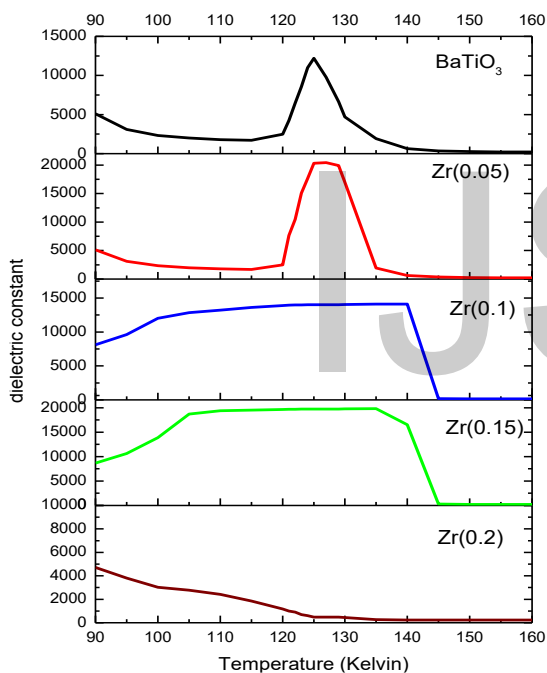
value as that of 0.05wt% but with a larger range of transition temperature 30^oC. Sample with 0.2 wt.% of zirconium is not showing any dielectric property.

3.5 LCR meter study

Parameters like resistivity and dissipation factor were studied using an LCR meter and is shown in figure 5(a-b). The variation of resistivity of samples with frequency is shown in figure 5(a), and it clearly indicates that electrical resistivity of the material decreases from high value to low value with increase in frequency independent of zirconium content. From the figure it is clear that all the samples with zirconium content were showing high resistance compare to the pure $BaTiO_3$. Rate of decrease of resistance with frequency is more as the amount of zirconium in the matrix increases. The dissipation factor (D) is a measure of loss-rate of energy. The variation of dissipation factor with frequency is shown in graphs below. It increases with frequency and then becomes saturated after a certain frequency.
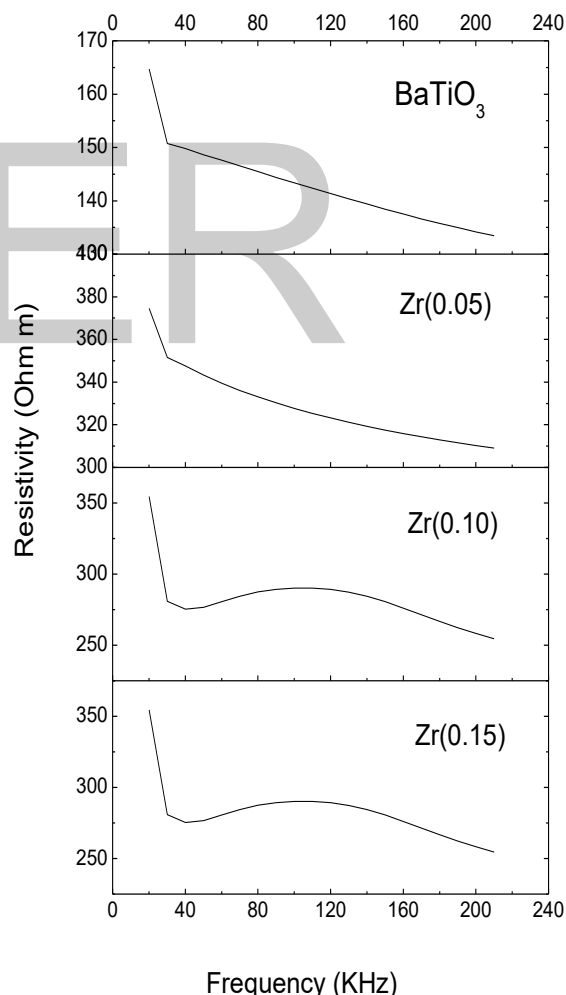

Figure 4: Curie temperature vs Dielectric constant of $Ba(Zr_xTi_{(1-x)})O_3(x=0,0.5,0.1,0.15,0.2)$

Table 3: Curie Temperature and Dielectric Constant of $Ba(Zr_xTi_{(1-x)})O_3(x=0,0.5,0.1,0.15)$

Sample	Curie Temperature(^0C)	Dielectric Constant
$Ba(Zr_xTi_{(1-x)})\ O_3$ (x=0)	125	12000
$Ba(Zr_xTi_{(1-x)})O_3$ (x=0.05)	125-130	20000
$Ba(Zr_xTi_{(1-x)})O_3$ (x=0.1)	100-140	14000
$Ba(Zr_xTi_{(1-x)})O_3$ (x=0.15)	105-135	20000

content further, the particle size started increasing again and the 0.15 wt% sample again showing the same dielectric

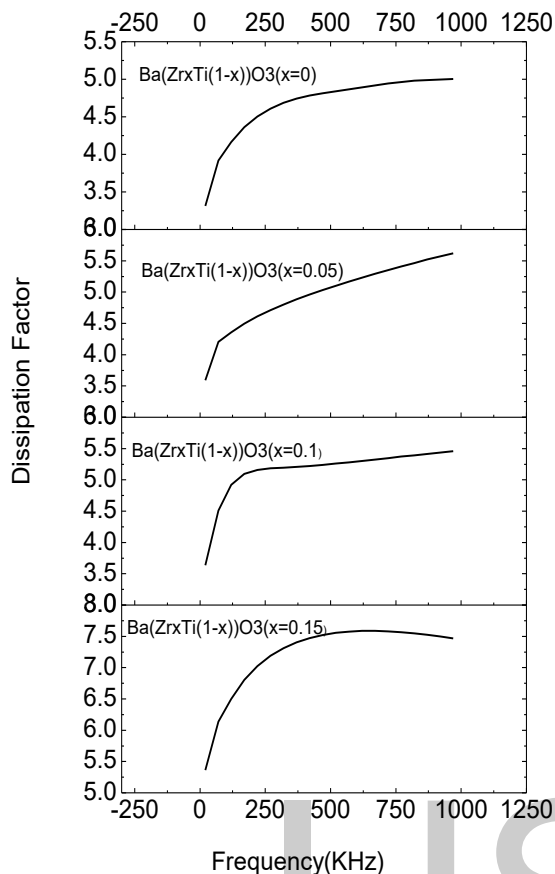**Figure 5(a) : Resistivity vs frequency of $Ba(Zr_xTi_{(1-x)})O_3$**

Figure 5(b): Dissipation factor vs frequency of $Ba(Zr_xTi_{(1-x)})O_3$

4. CONCLUSIONS

Even though the small amount of zirconium in the matrix does not change the phase formation, the particle size increases as the zirconium content increases. The increase in grain size is also confirmed by the SEM analysis. Another observation was, as the zirconium content increases it has broader dielectric constant peak and stronger frequency dispersion than that of the samples without doping. As the zirconium content increases more than 0.15 wt% its dielectric property started deteriorating. The sample doped with 0.05 and 0.15 wt% of zirconium exhibits the best dielectric property among the different zirconium doped samples and 0.15 wt% of zirconium doped sample exhibit widest dielectric constant than 0.05 wt% zirconium doped sample. Frequency studies were also carried out on the sample using LCR meter. Variation of parameters like dielectric constant, resistivity, and dissipation with frequency were also studied.

5. ACKNOWLEDGEMENT

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