

Influence of Seed Nano-Crystals on Electrical Properties and Phase Transition Behaviors of $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ Ceramics Prepared by Seed-Induced Method

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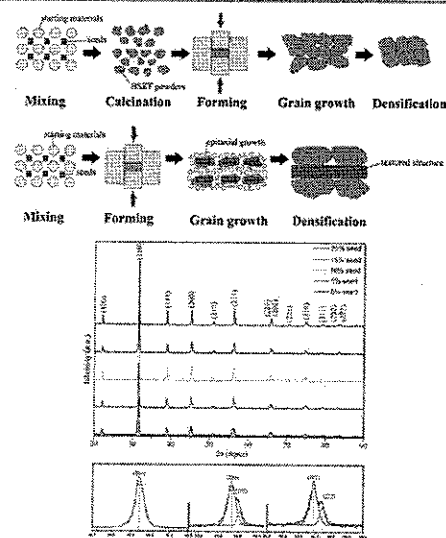
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This work studied the effects of seed nano-crystal on the electrical properties and the phase transition behaviors of $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ (BSZT) ceramics. The BSZT ceramics were prepared by the seed-induced method. The seed nano-crystal were prepared by the molten salt technique, and NaCl-KCl (1:1 by mole) eutectic mixtures were used as the flux.^[1] The ceramic powders were prepared by using a conventional method which added seed nano-crystals at various ratios. Results indicated that seed nano-crystals enhanced the electrical properties of ceramics. The sample with a 20 wt. % seed nano crystals has excellent value of dielectric constant (ϵ') of 34698 at maximum temperature. The phase transition temperature was observed at 60°C. The morphology was found that the grain size increasing significantly with an increased of seed nano crystals. The relaxor ferroelectric phase transition behavior was shown by a diffuseness parameter (γ). An increase in the BSZT-seed showed a decreased in γ value from 1.61 to 1.44. Thus the ferroelectric of the BSZT ceramics can be confirmed by hysteresis loop.

Keywords: BSZT ceramics, seed-induced, phase transition, dielectric constant



1. INTRODUCTION

Lead based perovskite ceramics for example PZT, PLZT and PMN-PT exhibited excellent properties, they can be used in a wide range of applications such as sensors, actuators, transformers, and energy harvesting.^[2-4] However, it has effects on the environment due to the volatilization of PbO during sintering process.^[3] Researchers are interested in developing new environmentally friendly materials. The lead-free BaTiO_3 based and $\text{BaZr}_{1-x}\text{Ti}_x\text{O}_3$ (BZT) ceramics are interesting as alternative materials to replace lead based ceramics.^[5-7] The lead-free ceramics have many reports for

the development structure, ferroelectric properties or to enhance the electrical properties as dielectric constants by adding or dopping some compounds such as SrCO_3 ,^[7] TiO_2 ,^[8] and MnO_2 ^[9] etc. or preparing the ceramic with more than one system such as the BZT-BCT (binary system).^[3,4] The ceramic process has many techniques such as sol-gel,^[10,11] molten salt method,^[12,13] and the conventional mixed oxide method.^[14,15] The different methods have effects on the structure as well as ferroelectric properties or electrical properties. Mahesh *et al.*^[4] was reported that the enhanced dielectric properties of $\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$ by using cold-isostatic pressing, the consisted of a high dielectric constant of ~14,000 at 1 kHz. In this work, we would like to introduce the seed-induced method for modifying the crystal phase to enhance the dielectric properties. This method combines the

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crystal-chemical, thermodynamics and kinetic of the reaction by $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ nucleus for the formation and stabilization of the phase. The nano crystal can be prepared by sol-gel, coprecipitation, hydrothermal etc..^[16-18] It is well known that the single crystal template growth under a controlled temperature condition could help to enhance the high electrical properties.^[19,20] Many researchers have carried out developing electrical properties of films by inserting a seed layer into a film preparation procedure for controlling the grain orientation and crystal orientation direction as well as improving the ferroelectric and piezoelectric properties of films.^[21,22] The addition of seed nano-crystals may play an important role in the powder preparation such as to increase the reactivity of precursor, the stabilization of perovskite phase, and the homogeneity of the solid solution. The perovskite phase can be formed at a lower calcination temperature; moreover, using the seed could improve the electrical properties of piezoelectric ceramics.^[23] In this study, the seed nano crystal was prepared by the molten-salt route. Then the seed was added to the starting materials for the induction of the $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ perovskite phase by solid state reaction. The structure, microstructure, dielectric properties and ferroelectric properties were investigated and discussed.

2. EXPERIMENTAL PROCEDURE

The $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ (BSZT) ceramic was prepared by the seed-induced method. The reagent grade metal oxide powders BaCO_3 (98.5%), ZrO_2 (99%), TiO_2 (99%) and SrCO_3 (99.9%) were used for starting materials. All of starting materials were purchased from Sigma-Aldrich and Aldrich, USA. The samples were prepared in two parts. First, BSZT nano-crystal seeds were synthesized from $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ powder by the molten-salt route. The precursor powders were calculated and weighed and then they were ball-milled for 10 h in ethanol with zirconia grinding media after that they were dried with the mixed powders. The powders were mixed with KCl-NaCl salt in the ratio of 1:1 (by mole) and calcined at 600°C, 700°C, and 800°C for 3 h. The nano-crystal seed was washed several times for removal of the salt with hot deionized water with examined remained Cl^- ions by silver nitrate titration then the powders were dried in an oven at 120°C. After that those seeds were examined their phase by x-ray diffraction.

Secondly, the BSZT nano-crystal seed of the pure phase perovskite were added to starting materials for preparation of the BSZT ceramics. The BaCO_3 , ZrO_2 , TiO_2 , SrCO_3 and BSZT nano-crystal seeds were mixed and ball-milled for 10 h in ethanol with zirconia grinding media, BSZT-seeds varied from 0, 5, 10, 15 and 20 wt. %, respectively. Next the mixed samples were dried. After that, the samples were calcined at 1200°C for 3 h, and then the calcined samples

were ground and pressed into a mold 10 mm in diameter. Finally, samples were sintered at 1400°C for 3 h. The scanning electron microscope (SEM) and intercept method were used to examine the microstructure and grain size. And phase formation observed by x-ray diffraction. The dielectric constant and dielectric loss of sintered ceramics were measured as function of frequency and temperature with an automated dielectric measurement system (Agilent E4980A LCR meter). After that the samples were characterized for ferroelectric properties by hysteresis loop using a precision workstation (Radiant technologies Inc.). The range in electric field of -30 kV/cm to 30 kV/cm was used.

3. RESULTS AND DISCUSSION

BSZT-seeds were prepared by the molten-salt route using NaCl-KCl salt with a 1:1 eutectic composition.^[1,24] The phase formation of the nano-crystal seed was analyzed by XRD as shown in Fig. 1. It was found that the sample calcined at 600°C and 700°C did not form pure perovskite phase. BSZT-seeds calcined at 600°C showing peaks of the starting materials, these peaks decreased when increasing the calcination temperature. The pure perovskite phase and their peaks corresponded to perovskite peaks at the sample synthesized at 800°C. Based on the JCPDS file no. 36-1880, it shows as the cubic structure. The nano crystal size and the morphology of the BSZT-seed were examined by using a SEM as shown in Fig. 2. It was shown that the SEM image and the size of the BSZT-seed is in the range of 146 ± 60 nm of cubic shape for samples that were synthesized at more than 700°C.

Results of phase formation and morphology indicated that the pure perovskite phase was found in the samples which prepared at 800°C. It was used as seed nano-crystals which added to the starting materials for inducing the reactivity of the precursor, homogeneity of the mixture and the form of perovskite phase increases.^[16]

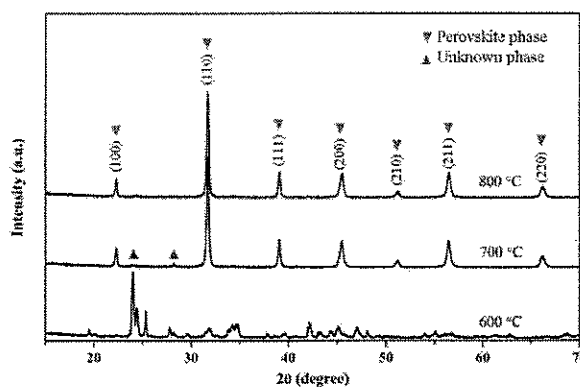


Fig. 1. X-ray diffraction patterns of BSZT-seed with varied the calcination temperature.

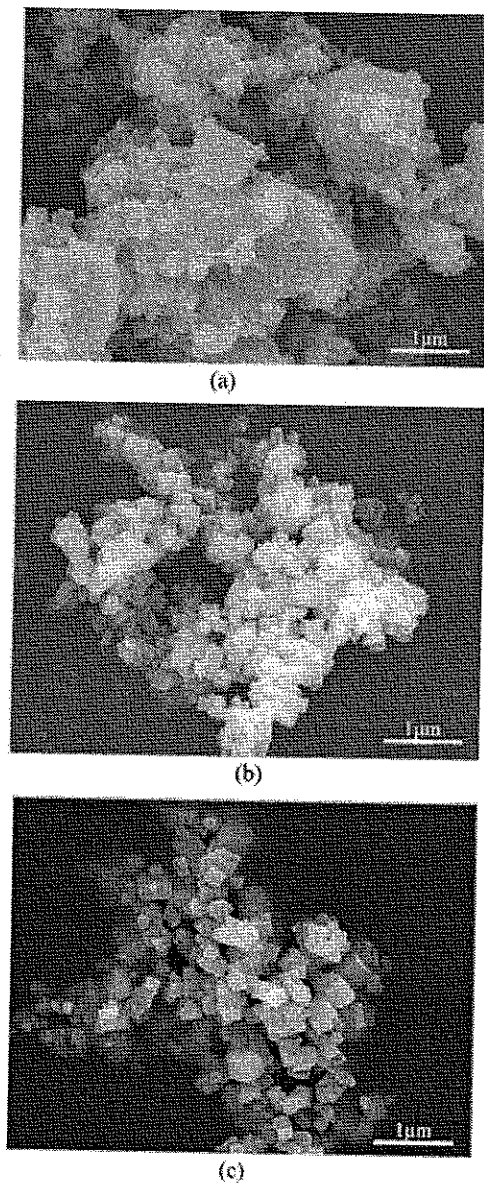


Fig. 2. SEM image of the BSZT-seed, (a) calcined at 600°C, (b) calcined at 700°C and (c) calcined at 800°C.

The x-ray diffraction patterns of the BSZT bulk ceramics were shown in Fig. 3. It was found that the XRD patterns show pure perovskite phase structure for all samples. The enlarged XRD patterns for $2\theta = 44^\circ - 46^\circ$, showed that the peak 200 while the pattern for $2\theta = 65^\circ - 66.5^\circ$ and $82.5^\circ - 85^\circ$ showed the peak split for 220/202 and 222/222. This result suggests that the ceramics show the existence of a rhombohedral phase, which is consistent with the work of Liu and Ren.^[25]

The morphology of the BSZT bulk ceramics were observed by scanning electron microscope. The SEM micrograph

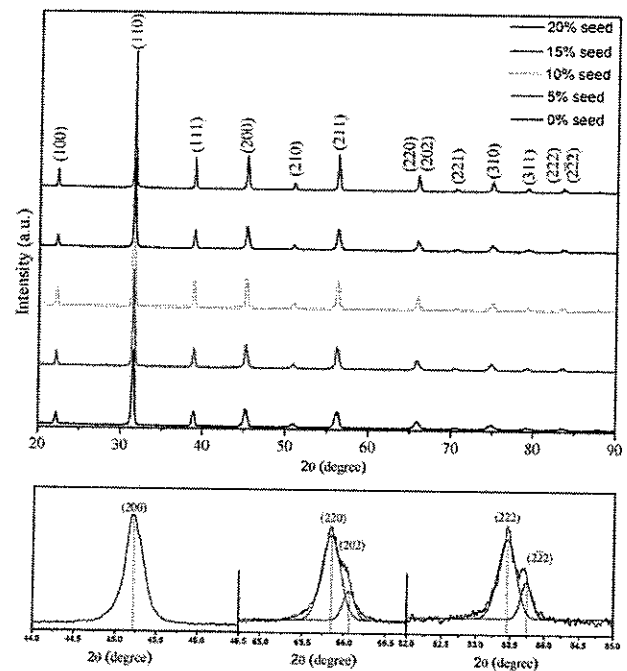


Fig. 3. X-ray diffraction patterns of BSZT ceramic prepared by seed-induced with varied the BSZT-seed concentration.

shown in Fig. 4, found that the grain size increased rapidly by increasing the seed nano crystals. This was due to the BSZT-seed acting as nucleus for the grain growth in BSZT ceramics as a function of phase nucleation.^[16] The grain size of the sample at 0% of BSZT-seed was $10.9 \pm 3.7 \mu\text{m}$, but when added BSZT-seed up to 20% the grain size increased to $74.4 \pm 54.8 \mu\text{m}$.

The grain size and density values of BSZT ceramics with varied BSZT-seed are shown in Fig. 5, the result shows that the density of samples increased with BSZT-seed nano crystal concentration, this can be confirmed by the SEM image. The density increased due to the grain size. Normally when the seed was added, it will induce phase formation by decreasing the energetic barrier for phase formation.^[16,18] The formation mechanism of higher seed quantity in BSZT ceramics can be explained by grain growth behavior as shown in Fig. 6. The random BSZT ceramics grains prepared by the seed induced method exhibit normal growth behavior same as the mixed oxide method, in which the higher the sintering temperature is, the bigger the grains become and the less the porosities exist. But for the template grain growth method (TGG) or textured grain growth method (TGG), the grain growth behavior is different. According to TGG reports^[26-30] the whole texture grain growth process can be divided into 3 steps in sequential order: (1) the phase formation stage, (2) the densification stage, and (3) the texture development stage. The grain size will be controlled by the amount of nucleation sites as well known. However, the seed induced

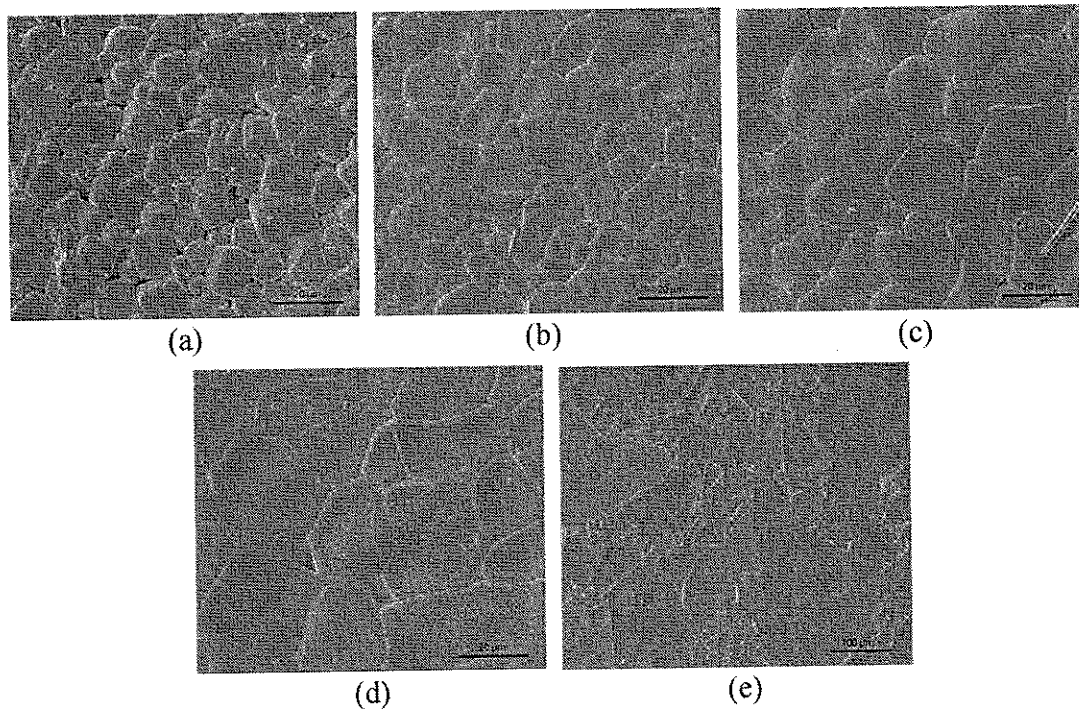


Fig. 4. SEM image of BSZT ceramic prepared by seed-induced with varied the BSZT-seed contained; 0% (a), 5% (b), 10% (c), 15% (d) and 20% (e).

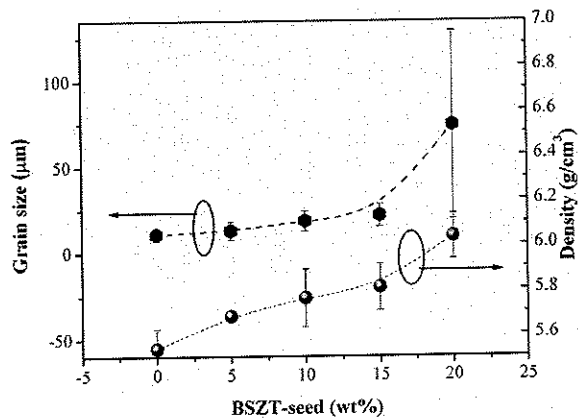


Fig. 5. The grain size and density values of BSZT ceramics with varied BSZT-seed contain.

method is different. At the stage of the phase formation. The seed provided framework for the anisometric BCZT grain form around the seed. We believed that the seeds helped to develop the phase formation process around itself. The BCZT formed far away seeds exhibited perovskite phase by normal solid state reaction. From the foregoing, it is therefore increase grain growth with increasing the number of seeds.

The dielectric constant (ϵ_r) with a difference in frequency depended on the temperature that was shown in Fig. 7. From the figure it was compared to the dielectric constant of the

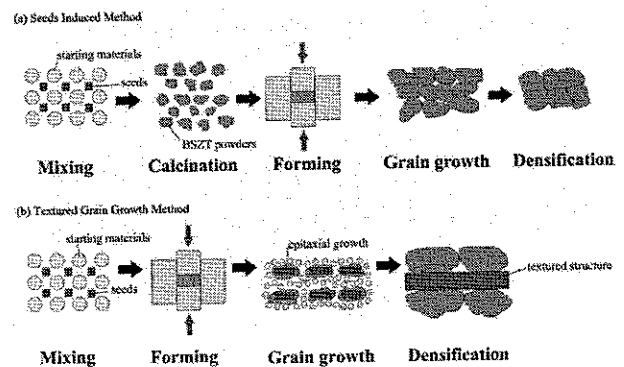


Fig. 6. Schematic diagrams of the growth mechanism in both Seeds induced method and textured grain growth method.

BSZT with variation in the BSZT-seed that contained from 0, 5, 10, 15 and 20 wt. %, respectively.

The result show that the maximum dielectric constant of the BSZT increased with increasing the BSZT-seed. At 0 wt. % of BSZT-seed the maximum dielectric constant of 7603 can be observed, while increasing the BSZT-seed up to 20 wt. % the maximum dielectric constant increased to 34699, this result due to the increasing grain size. It is well known that the dielectric constant depends on the composition, grain size, secondary phase, etc.^[31] The grain size of BSZT increased significantly when there was

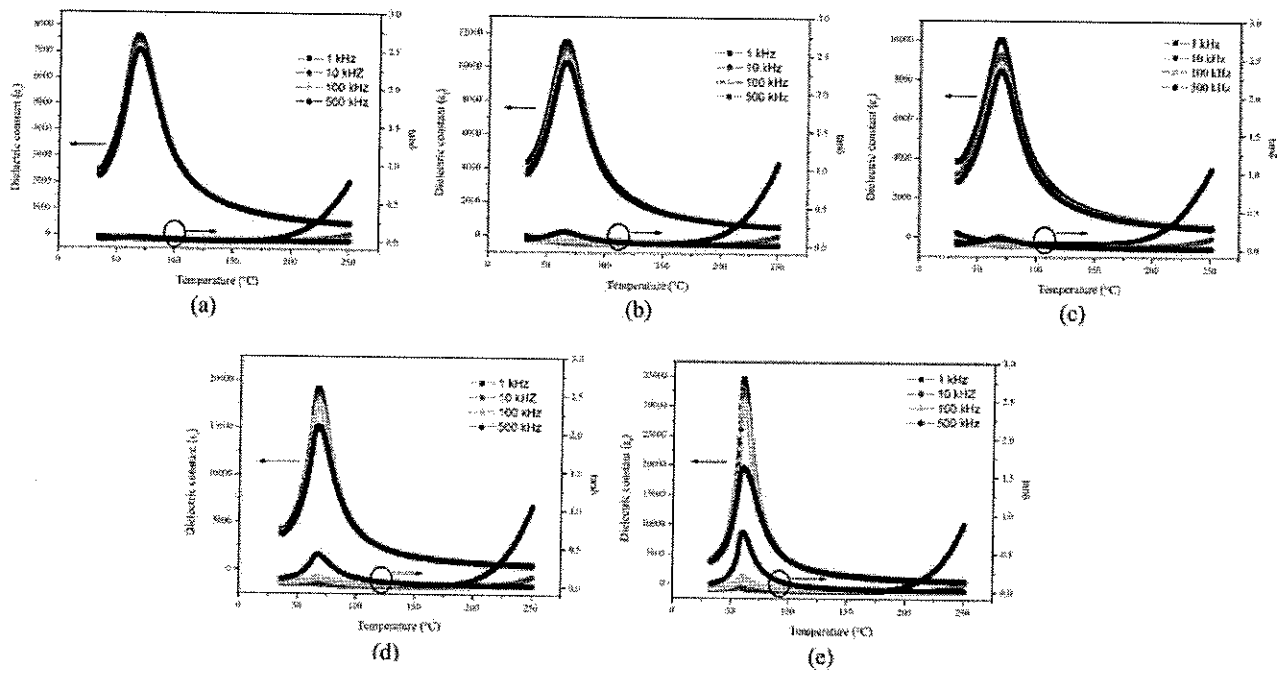


Fig. 7. Temperature dependences of dielectric constant of BSZT ceramics prepared by seed-induced method with varied the BSZT-seed, 0% (a), 5% (b), 10% (c), 15% (d) and 20% (e).

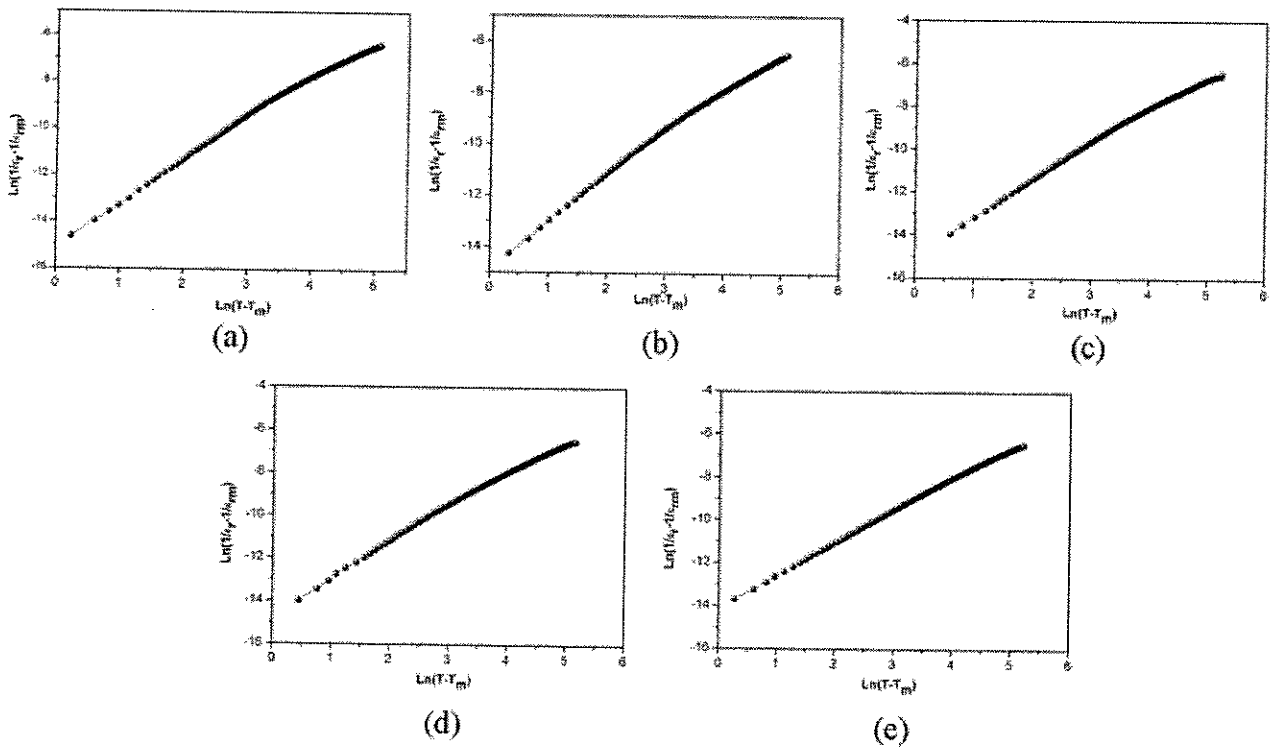


Fig. 8. $\ln(1/\epsilon - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ for BSZT ceramics measured at 1 kHz with varied the BSZT-seed contain, 0% (a), 5% (b), 10% (c), 15% (d) and 20% (e).

increase in the BSZT-seed. The higher grain size has effects on easier motion at the domain, which has result on the higher dielectric.^[31,32]

From the dielectric phase it can be characterization as a relaxor ferroelectric phase transition behavior. A diffuseness parameter can be calculated by using the modified Curie-Weiss relationship which is the law to explain the dielectric behavior of complex ferroelectric with diffuse phase transition.^[33] The diffuseness of phase transition shown by the γ value can be calculated from the equation (1).^[41]

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_{rm}} = \frac{(T - T_m)^\gamma}{K} \quad (1)$$

From this equation (1), ϵ_{rm} is the maximum dielectric constant, ϵ_r is the dielectric constant, K is a constant, for the ideal relaxor the amount γ value should be 2 and the γ value of classic ferroelectric of 1.^[34,35] The equation (1) plots the logarithm of this equation. The logarithm of this equation plots are shown in Fig. 8, with difference the BSZT-seed content. The slope of the curve is the γ value at 1 kHz. In this research, the γ values are decreased from 1.61 to 1.44 while increasing the BSZT-seed from 0 - 20 wt. %, respectively. Therefore the ferroelectric behavior increase related to

Table 1. Temperature of maximum dielectric constant (T_m), maximum dielectric constant (ϵ_m) and degree of dielectric relaxation (γ) of BSZT with varied seed content.

BSZT-seed (wt. %)	T_m (at 1 kHz) (°C)	ϵ_m	γ
0	68	7603	1.61
5	68	10087	1.51
10	65	11552	1.52
15	67	19159	1.49
20	60	34593	1.44

Table 2. Comparison of the electrical properties of lead free ceramics.

Composition	RT (1 kHz)		T_m (1 kHz)		D_{33} (pC/N)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	Ref.
	ϵ_r	$\tan\delta$	$\epsilon_{r,max}$	T_c (°C)				
$\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$	5510	0.009	-	-	-	-	-	36
$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$	3800	0.025	16000	100	-	-	-	37
$\text{Ba}_{0.80}\text{Sr}_{0.20}\text{TiO}_3$	2000	-	8000	50	-	-	-	38
$\text{Ba}_{0.85}\text{Sr}_{0.15}\text{TiO}_3$	1000	0.022	2320	78	-	0.87180	1.4176	39
$\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$	-	-	-	-	300	-	-	40
$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Zr}_{0.04}\text{Ti}_{0.96}\text{O}_3$	4000	0.07	20000	90	-	-	-	37
* $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$	2495	0.044	7603	68	39.4	5.14	5.03	0 wt. %
	3885	0.054	10087	68	168	5.24	2.37	5 wt. %
	4351	0.081	11552	65	138	5.84	1.33	10 wt. %
	4332	0.040	19159	67	145	6.42	1.21	15 wt. %
	4000	0.031	34593	60	111	3.78	1.33	20 wt. %

* $\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ prepared by seed-induced method with difference content BSZT- nano seed.

BSZT-seed content. T_m , ϵ_m and the γ value was shown in Table 1.

In Table 1 Temperature of the maximum dielectric constant (T_m), maximum dielectric constant (ϵ_m) and degree of dielectric relaxation (γ) of BSZT with variation in seed content and electrical properties are comparable with the results of previous works that are shown in Table 2. It was found that the electrical properties of BSZT ceramics prepared by the seed induced method were increased when it was compared to the compound nearby.

In addition, the plots of a dielectric constant as a function of electric field with variations in the BSZT-seed content are displayed in Fig. 9. The BSZT varied in seed content from 5, 10, 15 and 20 wt. %, respectively. The applied electric field was used in the range of -25 kV/cm to 25 kV/cm. From the dielectric constant-electric field plots it can be calculated in the relative tunability (n_r) by the following equation (2).^[33]

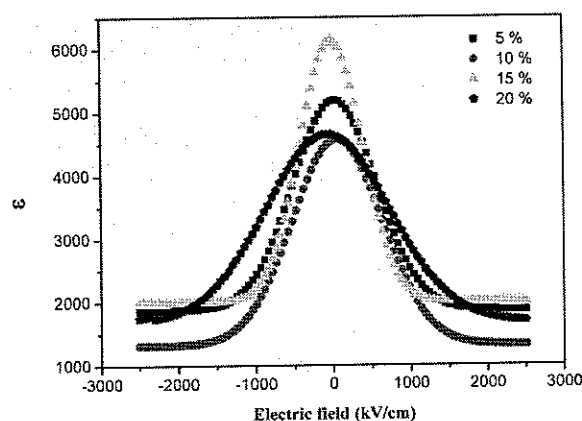


Fig. 9. Dielectric constant as a function of electric field with varied the BSZT-seed contain.

$$n_r\% = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \times 100 \quad (2)$$

Where, $\varepsilon(0)$ and $\varepsilon(E)$ are the dielectric constants at zero of the electric field and the dielectric constant at higher electric field, respectively. The n_r compared with the BSZT-seed contains Plots in Fig. 10. The result shows that n_r values were 64.2%, 71.3%, 67.5%, and 64.0% at the BSZT-seed from adding 5, 10, 15 and 20 wt. % respectively and the high relative tunability was observed at 10 wt. % of BSZT-seed contents.

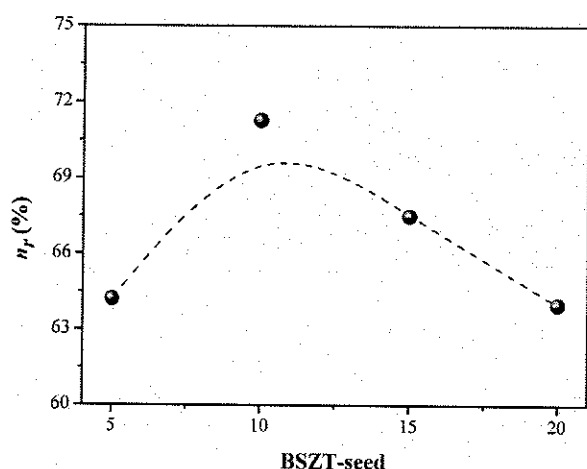


Fig. 10. Relative tunability versus difference BSZT-seed contain.

The ferroelectric properties of the BSZT ceramics prepared by the seed-induced method can be confirmed by a hysteresis loop. The hysteresis loops of the samples were measured by using a precision workstation system, that is the function of polarization (P) and an applied electric field (E) show in Fig. 11.

From the hysteresis loops show the slim hysteresis loop. The hysteresis was given the remnant polarization (P_r), saturation polarization (P_s) and the coercive field (E_c) that is shown in Table 2. The P_r and P_s of the samples increased from $5.16 \mu\text{C}/\text{cm}^2$ and $6.0 \mu\text{C}/\text{cm}^2$ to $6.42 \mu\text{C}/\text{cm}^2$ and $10.6 \mu\text{C}/\text{cm}^2$ with an increase in the BSZT-seed from 0 - 15 wt. %. The increase in the P_r was mainly due to better homogeneity and uniformity of the grain size.^[36]

When increased the BSZT-seed to 20 wt. %, the P_r and P_s decreasing to $3.78 \mu\text{C}/\text{cm}^2$ and $6.8 \mu\text{C}/\text{cm}^2$ respectively. This result may be attributed to the non-homogenous of the grain growth as presented in the sample. Abnormal grain growth occurred in 20 wt. % ceramic seeds probably the result of salt left in the process of preparing the seed. Remaining salt cannot be identified because of limitation of instruments. The remaining salt can serve as a sintering aid and caused abnormal grain growth in ceramics sintered as it is well know. It can be observed that the dielectric performance increased rapidly, probably as a result of salt remaining due to the loss tangent increase. The dielectric constant changed dramatically as the frequency becomes higher. The hysteresis loop also exhibit lossy capacitor.

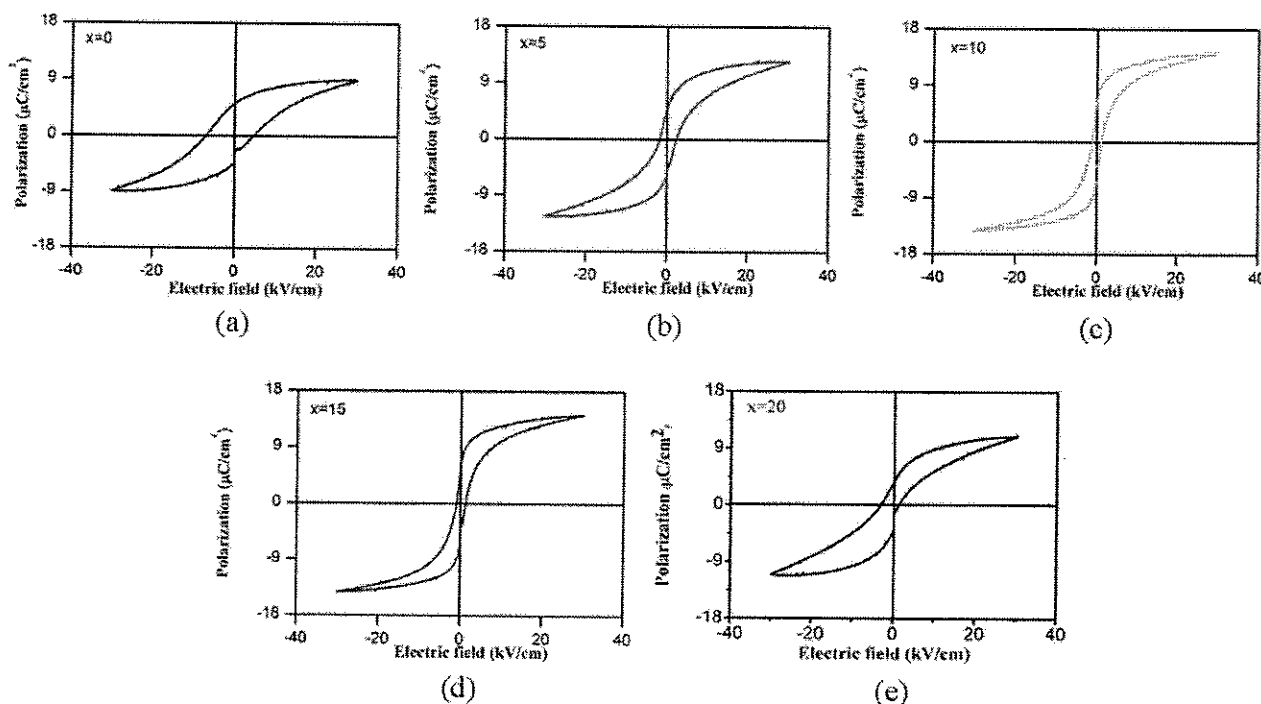


Fig. 11. Hysteresis loop of BSZT with varied the BSZT-seed contain.

Table 3. The remnant polarization (P_r), saturation polarization (P_s) and the coercive field (E_c) of BSZT ceramics with varied seed contain.

PSZT-seed (wt. %)	P_r ($\mu\text{C}/\text{cm}^2$)	P_s ($\mu\text{C}/\text{cm}^2$)	E_c (kV/m)
0	5.14	6.0	5.03
5	5.24	8.5	2.37
10	5.84	10.3	1.33
15	6.42	10.6	1.21
20	3.78	6.8	1.33

After considering the E_c , it was found that the E_c decreased as the BSZT-seed was added in to BSZT-based ceramics. Large grain size plays an important law for this reduction of E_c . Generally, ferroelectric material with large grain size exhibited low E_c whereas high E_c was observed in smaller-grained materials; therefore, lower E_c was found in samples with added BSZT-seeds.^[13] The P_r , P_s and E_c summarized in Table 3.

4. CONCLUSIONS

$\text{Ba}_{0.85}\text{Sr}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ ceramic prepared by the seed-induced method with varied BSZT-seed nano crystals. It was shown that the grain size and density increased with increasing the BSZT-seed nano crystals. The grain size of the sample increased from $10.9 \pm 3.7 \mu\text{m}$ to $74.3 \pm 54.8 \mu\text{m}$. The non-added seeds, the maximum dielectric constant of 7603.4 can be observed when increasing the nano-seeds up to 20 wt. % with the maximum dielectric constant increasing to 34698.6, this result is due to the increase in grain size. The γ value of the samples decreased from 1.61 to 1.44 with an increase in the BSZT-seed nano crystals content which is shown in the characteristics of diffuse ferroelectric behavior, and is consistent with dielectric behavior. Therefore the ferroelectric behavior increase was related. The ferroelectric of the BSZT ceramics were observed by the hysteresis loop. The results show that P_r and P_s of the samples increased from $5.16 \mu\text{C}/\text{cm}^2$ and $6.0 \mu\text{C}/\text{cm}^2$ to $6.42 \mu\text{C}/\text{cm}^2$ and $10.6 \mu\text{C}/\text{cm}^2$ with the increase of the BSZT-seed from 0 - 15 wt. %. The increase in the P_r was mainly due to better homogeneity and uniformity of grain size. However, as the BSZT-seed increased to 20 wt. %, the P_r and P_s decreased to $3.78 \mu\text{C}/\text{cm}^2$ and $6.8 \mu\text{C}/\text{cm}^2$ respectively. This result may be attributed to non-homogeneity of grain size as presented in the sample. The E_c decreased as the BSZT-seed was added in to BSZT-based ceramics. This is an effect of the large grain size that plays an important law for reduction of E_c . From this research the seed-induced method is the one of many interesting methods because this method can modify the crystal structure and reduced the temperature for phase formation and can improve the dielectric constant.

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