The Electrical Hysteresis Loop and Polarization Value of $BaZr_xTi_{1-x}O_3$ Multilayer Films Material at Different Annealing Temperature (x = 0.1 and 0.08) based on Sawyer Tower Circuit

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Abstract

The crystallographic properties and ferroelectric state of BZT multilayer films which deposited on Si (100) substrate was studied in this work. XRD pattern peaks show that $BaZr_{0.1}T_{0.9}O_3$ and $BaZr_{0.08}Ti_{0.92}O_3$ are found well-crystallized at 800^oC for 3 hours corresponding to vary annealed temperature. The BZT multilayerfilms are identified as tetragonal-perovskite structure. This is supported by the existence of a measured hysteresis loops which the instrument and the system is on own works.Fundamentally of theoretical in physics field, the Sawyer-Tower Circuit has been concluded to ferroelectric phenomenon analysis on sample of material with experimental result as P-E hysteresis curve.The Sawyer-Tower Circuit method was used to measure the electrical polarization with triangle wave signal at fixed frequencies 50 Hz(ϕ = 0), and maximum electrical field (E_{max}) were injected continuously at the 40 Volt/cm. The system plotted the electrical field with respect to polarization (P-E curves), include its value. This data was used as a parameter for determining electric property of material. These results have shown the maximum value of electric field which could be used as measurement parameter. The highest maximum polarization, 34.12 $\mu C/cm^2$, have been determined and obtained on $BaZr_{0.1}T_{0.9}O_3$ at 800^oC for 3 hours annealing process and its maximum electric field is noted to be about 38.3 Volt/cm on all samples.In the normal manner,theresultcan provide an explanation of polarization and electrical behavior of ferroelectric sample for further research.

Keywords: $BaZrTiO_3$, crystallite size, Sawyer-Tower, hysteresis loops, polarization

1. Introduction

Ferroelectric ceramics are identified by its reversible spontaneous polarization. This property is well known for memories, solar cell, and sensor application. Lead-based materials, such as PZT, have great impact in applications, such as ultrasonic transducer[1]. In spite of its advantageous, lead has a hazardous characteristic for environment. As the regulation of European directive RoHS (Restriction of Hazardous Substances, 2002/95/CE) released, lead is prohibited in electronic devices. Barium titanate, $BaTiO_3$, is a lead-free oxide andelectro materials which is mostly high studied in some research because of its electrical properties, such as ferroelectric properties[2]. Ferroelectric oxides, perovskite-based, have high dielectric constant and electromechanical coupling coefficient[3]. However it still remains the leakage current and dielectric loss. Therefore modifications in barium titanate always become interesting to be developed.

The research of ion substitution into structure is still in progress to find the best characteristics of barium titanate, since the substitution of other ions on ABO_3 structure will change its characteristics[4]. *Vijatovic* studied the influence of lanthanum doped $BaTiO_3$ and stated that lanthanum is improving the dielectric properties[5]. One of promising element is zirconium, in which the ions can be replacedothers ions in B-site of perovskite structure $BaTiO_3$[6,7]. The formation of Barium Zirconium Titanate ($BaZrTiO_3$-BZT) is interesting, because the Zr substitution, like Sr, tend to decrease and shift the Curie temperature[8]. Because of Zr^{4+} ion is more stable than Ti^{4+} ion, giving an effect to depress and maintain the low and stable leakage current of $BaTiO_3$[9]. As the zirconium ion increase 20%only cubic phase exists[10]. Kajtoch confirmed that Zr ion substitution is directed to strong diffuseness and lowering paraelectric-ferroelectric transition[11]. In the vicinity of room temperature, the BZT ($0<x<0.20$) is ferroelectric phase[12]. Nanakorn et al stated that in the mixed-method, an optimum heat treatment, such as sintering, could affect the ferroelectric behavior[13]. Thus in our present study, we focused on the ferroelectric behavior of BZT under circumstances of different annealing temperature.

The basic principles of Sawyer-tower circuit can be performed to high-optimum result for characterization of ferroelectrics phenomenon. It will alsogeneratethe classification of electrical behavior of hysteresis on material.This is atype of low-cost instrument devices for ferroelectric elements[14].The basics method of this circuit has been optimized to measure a spontaneous polarization, remnant polarization, coercive field and polarization reversal mechanism[15].

2. Method

This part of description about fundamental method for electronics measure element that was designed from basic configuration uses anoriginal Sawyer-Tower circuit. Basically from this circuit,P-E curve standard parameters can be plottedto interpretelectrical characteristics and also be predicted thepolarization value and order area of materials. The basic standard configuration of probe has been madefor thin films material with mechanism of two probes to injectthe elements of electrical field into the sample and afterwards measure voltage load of sample (capacity voltage of sample).

Thin substrate and probe configuration are very important.It must be appropriate to measure the data from material to be efficient and precise. This research picked out Si-substrate element (in the thickness of 900 nm). The polarization and the electrical field injection can be plotted pass through/by means of probe.The optimized-probe was selected to the implementation of Sawyer-Tower circuit on behalf of ferroelectrics material characterization process.

The schematics setup with capacitor configuration has been developed by Sawyer-Tower.The system obtains ferroelectrics parameter phenomena with data results of P-E curve. The original Sawyer-Tower circuit is a very practical circuit for hysteresis loops. Besides, it is useful for the material, which has a low loss and high polarization. Fig 1. presents the original S-T circuit for tracking a hysteresis loops of ferroelectric material.

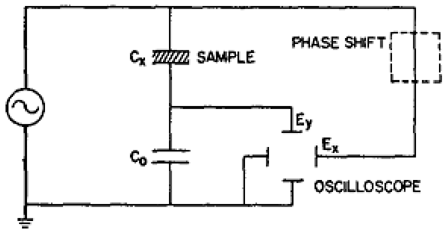

Fig. 1. The Original Sawyer-Tower circuit for measuring a sample of material[15].

This schematic of circuit capacitor, as shown on Fig 2, pervade a two capacitance model (C_x = Capacitance ofsample, and C_{sense} = Capacitance of sense). In the rules, C_{sense}has a bigger capacitance value as compared to C_x of sample tested. The element of capacity variable of C_x is the ferroelectric sample to be the measured area, and C_{sense} is a reference capacitor of a well known capacity that is constant and independent of the applied voltage.

The measuring circuit elements is supplied with a triangle wave electrical signal voltage U_{ac}, and also as for to display the PE-curves to the oscilloscope XY display panel. The X-channel gets display an electricalfield (E – inside of the sample of material – C_x variable) with proportional equal with voltage injected into the sample (voltage sample C_x). Whereas, The Y-channel is a voltage which proportional to the electrical polarization P of the sample tested. Both voltages have to be referred to the same value of electrical potential parameter.The input impedance of the oscilloscope is high enough in comparison to all resistances and impedances of the circuit so that we do not have to take it into account.

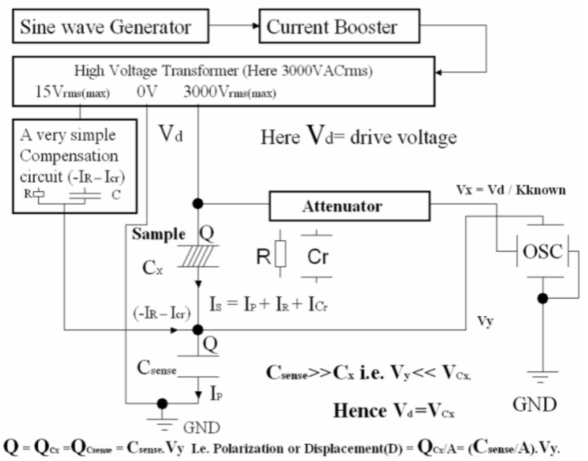

Fig. 2. The Schematic of configuration setup the Sawyer-Tower circuit for measuring a sample of material[15].

Fig. 3 shows the basic principle of inner circuit of the Sawyer-Tower with voltage signal input generator, matching impedance trafo (step-up AC voltage) and so the capacities can be switched with the help of switch (S_w) to find a compromise value of capacitance. The capacitance selection construe C_x variable in Sawyer-Tower circuit with compromise a neglecting voltage drop.

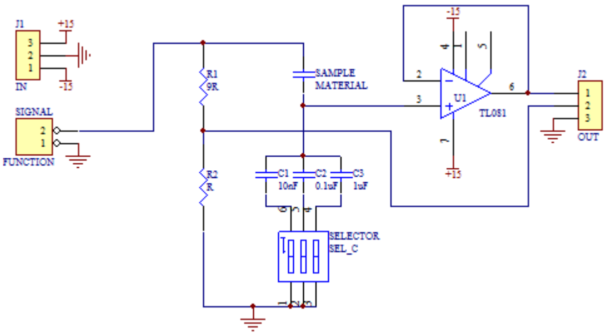

Fig. 3. Sawyer-Tower circuit for capturing P-E value with buffer based on Operational-Amplifier Device

Some system applies the electric field at fixed important value of 50-60 Hz[14,16].Its systems invert the drive signal by using the op-amps and furthermore itgenerates $-I_R$ and $-I_{Cr}$. Those current isadded up with the whole current to determine only polarization current that is united to give polarization as voltage property. In this system we implemented modification circuit with Op-amp IC device accompanying electrical buffer mechanism as shown on Fig 3.

As previous study done by Bouregba, it allows us to remove the possible loop deformations through a numerical compensation acting as a modified Sawyer–Tower circuit[17]. The relevance of ferroelectrics and S-T circuit can be influenced by the thickness of films. The reducing of thickness on films typically comes with an apparent degradation of their dielectric and ferroelectric properties[17]. Low oxygen concentration in the film and fatigue, which are known to increase leakage current, induce observable shifts[18].

3. Experimental Procedure

3.1. *Preparation of BZT ceramics*

Crystalline $BaZr_xTi_{1-x}O_3$($x = 0.08$ and 0.1) ceramics multilayer films were prepared from alkaline acetates such as barium acetate ($Ba[CH_3COO]_2$, Sigma Aldrich,99%], zirconium n-butoxide ($Zr[C_{16}H_{36}O_4]$, Alfa Aesar, 88%), and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$, Sigma Aldrich, ≥ 97%) in high purity. In the ratio 3 to 1, acetic acid (CH_3COOH, Merck KGaA, 100%) and ethylene glycol ($C_2H_6O_2$, Merck KGaA, ≥99.5%) were used as solvent agents[19]. Ba-solution was prepared by continuously stirring barium acetate in warm acetic acid at 80°C for 1 h. Stoichiometric amount of titanium isopropoxide and zirconium n-butoxide were added according to a predetermined ratio 92/8 and 90/10 into barium solution. After the solution is well mixed, ethylene glycol was added in final step to stabilize and bind more complex bond in solution.

The CSD sol-gel process is followed by spin coating could produce ceramic films, as described previous[20]. The spin coating process was done by dropping and deposited the BZT solution on cleaned (100)-oriented Si substrate. Furthermore it was rotated at 3000 rpm for 30 s[21]. The films were fired at 300°C for 5 min in order to lose the organic phase and also as pre-crystallization process. The process of substrate's depositing, coating, and firing were repeated until the desired of layers is achieved. The samples were annealed at 700°C, 800°C, and 900°C for 3 h.

3.2. *Characterization*

The crystallographic structure was characterized by X-Ray difrraction using a Phillips Analytical PW371 diffractometer with Co-Kα (λ = 1.79 Å). Rietveld refinement was done to estimate the change of lattice parameter. Crystallites size of BZT films were estimated using Williamson-Hall method. The hysteresis loops, which is one of indicator for ferroelectric properties, was carried out using a Sawyer-Tower Circuit Standard Model[15].

The films are exposed by "Triangle Wave Signal" (Alternating-Current signal) with frequency 50 Hz and maximum voltage peak on 50V (ϕ = 0). The data has been plotted with P-E curve standard graph model which is side by side with the Triangle Signal Wave-plotting as can be observed at Fig. 5. That signal can be represented as parameter of injection voltage to the films and load voltage measure of reference capacitor for Digital Oscilloscope (data saved via USB communication).

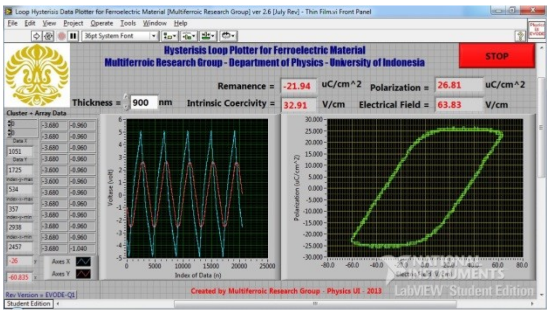

Fig. 5. The Data Plotter for determining the ferroelectric properties

The data can be calculated with standard algorithm for determining remnant polarization (P_r), maximum polarization (P_m), maximum electric field (E_m), and coercive field (E_c) from data cluster/array which is taken from experimental data. Basically, the capacitance of reference capacitor is absolutely important to calculating those experimental data. The response of circuit mechanism of capacitance couple can be represented of sample polarization and triangle signal was displayed if the sample has been polarized. The deformation of phase and load voltage can be analyzed as the value of sample polarization and injection voltage as electrical field.

4. Result and Discussion

4.1. *Crystallographic Results*

The XRD patterns for all samples refer to the well-crystallized of BZT films as can be seen in Fig 1. The BZT films were annealed at 700°C, 800°C, and 900°C for 3 hours at the heating rate 10°C/min. Diffraction pattern revealed the polycrystalline perovskite tetragonal structure which is identified by matching it in Crystallography Open Database (COD No. 96-210-0861). It can be observed that the pattern represent (100), (110), (111), and (200)-oriented perovskite peaks.

Slightly the change of Si substrate peak from 800°C to 900°C is identified; exclude the film that annealed at 700°C. The less annealing temperature in crystal growth clouds Si peaks. Furthermore, even Si substrate peaks is observed, no other obvious impurity phases are found besides BZT phase. Both $BaZr_{0.08}Ti_{0.92}O_3$in the Fig. 6and $BaZr_{0.1}Ti_{0.9}O_3$, in the Fig. 7, also shows an optimum temperature of crystal growth of BZT ceramics is 800°C. It may arise as the effect of annealing process in crystallization. Relative high background intensity in all BZT films is considered as the using of Co-source in XRD.

In the fact that the ionic radius of Ti^{4+} ions is smaller than Zr^{4+} ions, the substitution of Zr^{4+} ions in Ti^{4+} (B-site) could increase the lattice parameter, as can be observed in Table 1. The more addition of doping parts may expand their unit cell in crystals. Another consideration that might be taken in role is the ratio c/a which represent as the tetragonality of crystal structure. The rising of the c/a value means that the displacement of Ti/Zr in B-site bigger corresponds with its centrosymmetric site. This caused a defect in structure which was compensated by oxygen vacancies. Theoretical calculations have shown by Khatib that the contribution of the oxygen ion would affect electronic polarizabilities of material[22]. Mihara et al also explained about the creation of oxygen-deficient layers because of electric field cycling[23].It may pointedout that some ferroelectric crystals characterization may give the contributions deform the hysteresis loops.

Table 1. The crystal structure and ferroelectric properties of BZT films.

Properties	BZT7(08)	BZT7(10)	BZT8(08)	BZT8(10)	BZT9(08)	BZT9(10)
a (Å)	3.993	4.014	4.006	4.022	3.998	3.998
c (Å)	4.033	4.047	4.015	4.094	4.026	4,032
c/a	1.010	1.008	1.002	1.018	1.007	1,009
Crystallie Size (nm)	53.22	84.14	75.26	118.99	56.09	84.14
P_m ($\mu C/cm^2$)	28.43	30.87	31.68	34.12	27.62	31.68
Pr($\mu C/cm^2$)	20.31	25.19	23.56	21.12	21.94	21.94
Ec(V/cm)	19.15	17.95	17.95	14.96	19.75	16.16
E_m(V/cm)	38.3	37.7	38.3	38.3	38.3	38.89

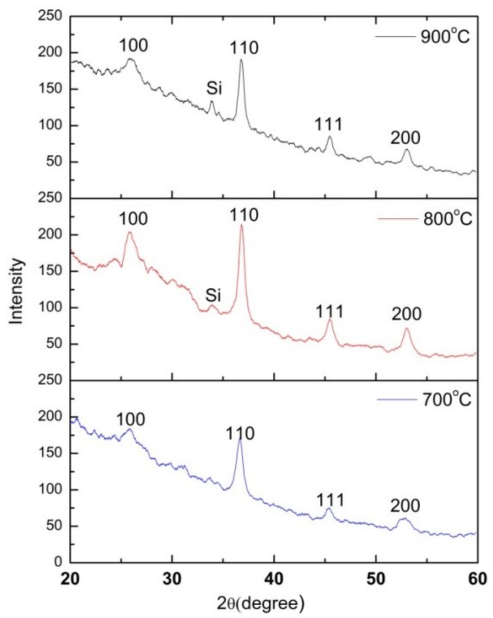

Fig. 6. XRD pattern of BZT ceramic films for 5 multilayers with $BaZr_{0.08}Ti_{0.92}O_3$

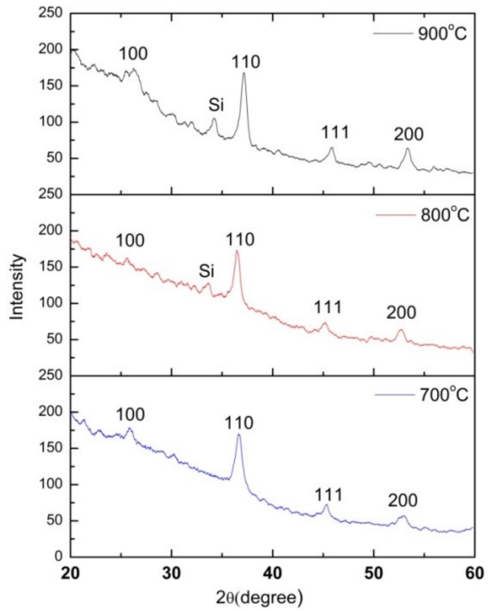

Fig. 7. XRD pattern of BZT ceramic films for 5 multilayers with$BaZr_{0.1}Ti_{0.9}O_3$

4.2. Ferroelectric Results

The Sawyer-tower circuit has been used to measure the values of the ferroelectric parameters of BZT films. BZT multilayer films showed well defined the properties of ferroelectric. The P-E hysteresis loops of samples as the function of annealing temperature are shown in Fig 8 and 9. The nature of sample voltage in y-axis represented as polarization of the material, while x-axis as electric field. The shaping of S-curves itself is related with P-E relation non-linearly due to the ferroelectric perovskite structure. The maximum polarization of $BaZr_{0.08}Ti_{0.92}O_3$ and $BaZr_{0.1}Ti_{0.9}O_3$ films are found to be increasing from 700°C to 800°C, but slightly decrease when the temperature is 900°C as can be observed at table 1.

Among of different annealing temperature, the $BaZr_{0.1}Ti_{0.9}O_3$ ceramic has the highest maximum polarization at 800°C, P_m = 34.12 $\mu C/cm^2$. This is also followed by the $BaZr_{0.08}Ti_{0.92}O_3$ ceramics with polarization 31.68 $\mu C/cm^2$. This value may arise from the different of crystallite size as well reported by Cheung[24].

The average crystallite size of BZT films were found to be about less than 120 nm. Fig 10. shows the graph of $BaZr_{0.08}Ti_{0.92}O_3$ and $BaZr_{0.1}Ti_{0.9}O_3$ films of annealing temperature-dependent. Crystallite ceramics, for both Zr-doped, which is annealed at 800°C, have the biggest size rather than other temperature for each concentration of Zr ions. It describes the growth of crystallite as the function of annealing temperature. The relation between crystallite size and grain size allow us to find the influence of crystallite size for polarization. We observed an increasing or decreasing of the polarization is affected by its crystallite size. The increase in polarization value could be associated to the increase in crystallite sizes. Similarly condition was achieved by Chen in the term of grain size[25].

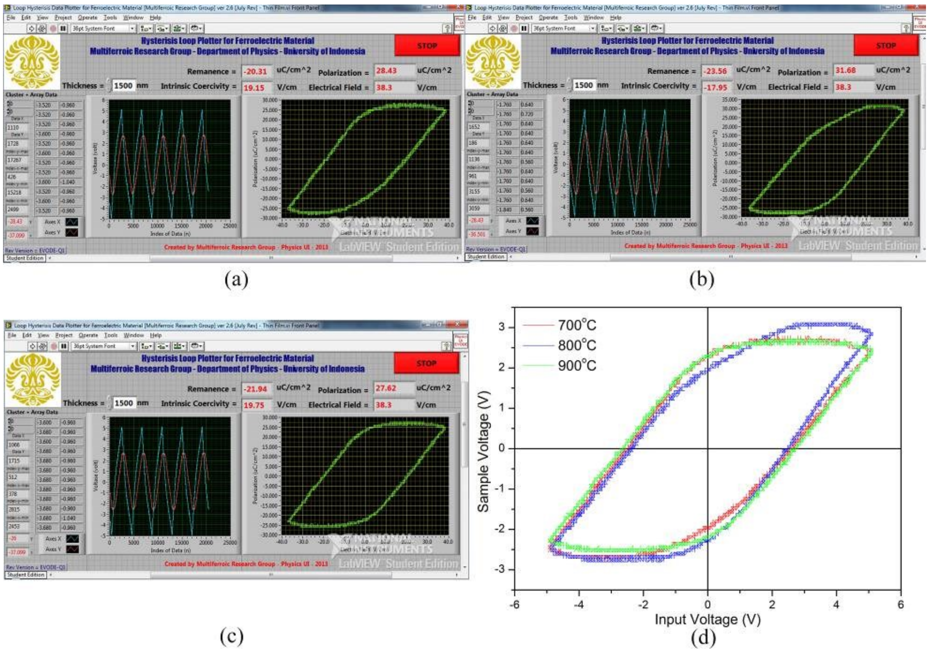

Fig. 8. Hysteresis loops plotting of $BaZr_{0.08}Ti_{0.92}O_3$ films, annealed at(a) 700°C, (b) 800°C, (c) 900°C, and (d) well-mixed hysteresis samples in *voltage*.

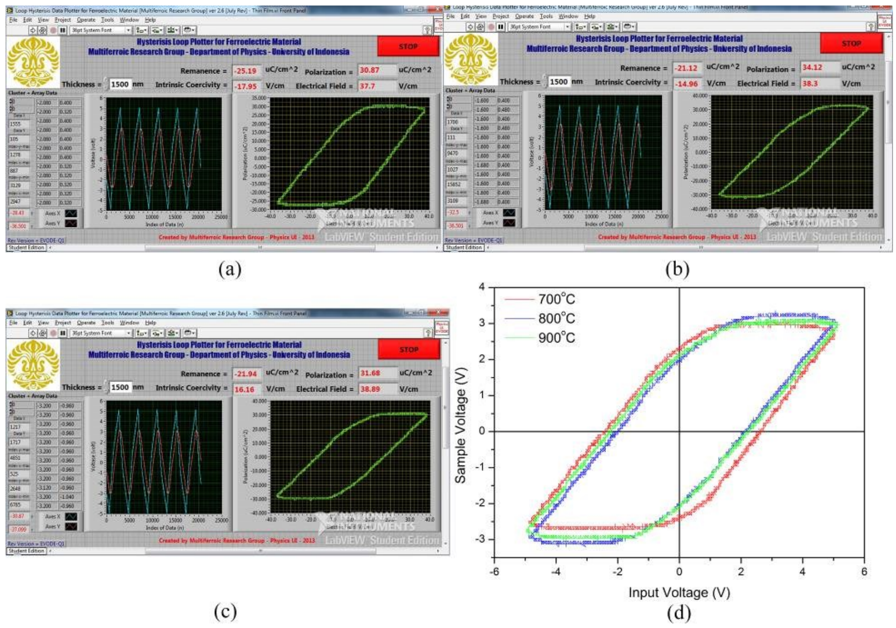

Fig. 9. Hysteresis loops of $BaZr_{0.1}Ti_{0.9}O_3$ films, annealed at (a) 700°C, (b) 800°C, (c) 900°C, and (d) well-mixed hysteresis samples in *voltage*.

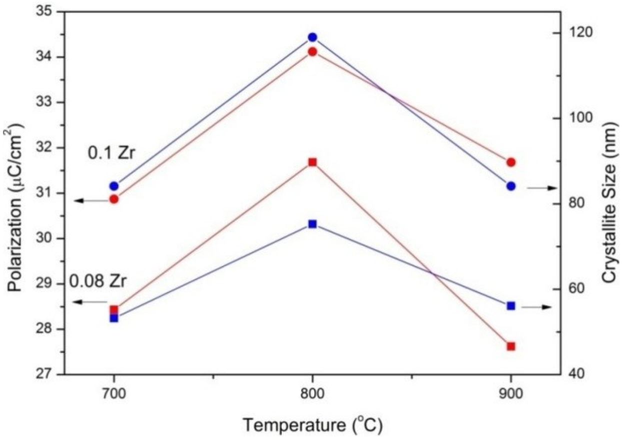

Fig. 10. Graph of BZT films properties depend on annealing temperature. (Left axis) maxima polarization and (right axis) crystallite size

This may arise as the grain size increases; the number of grain boundaries decrease. The result of grain boundaries decrease will cause an increasing of polarization value, because the grain boundary has a low permittivity. Another factor that may be included is the existence of space charge in the grain boundary which causes the depolarization field[26]. This similar phenomenon has also been observed by Didier et al on BTS films[20].In As we compared, $BaZr_{0.1}Ti_{0.9}O_3$ have a larger size and higher polarization than $BaZr_{0.08}Ti_{0.92}O_3$.

The remnant polarization of $BaZr_{0.1}Ti_{0.9}O_3$ ceramics, which is done by Bhaskar, showed the lower P_r as we compare with our studies[27]. In our study, the remnant polarization of $BaZr_{0.1}Ti_{0.9}O_3$ is to be found higher 21 $\mu C/cm^2$ for all temperatures. With the increase in Zr content, 0.08 to 0.1, the material softens which is indicated by the reduction in coercive field (E_c). At 800°C sample, the coercive field decrease from 17.95 V/cm ($BaZr_{0.08}Ti_{0.92}O_3$) to 14.96 V/cm ($BaZr_{0.1}Ti_{0.9}O_3$). Parveen also explained the coercive field as the function of Zr content[2]. It can be explained that for all samples the maximum electrical field relatively constant to be noted approximately 38 V/cm.

5. Conclusion

The XRD pattern shows that ferroelectric tetragonal-perovskite phase BZT films were produced by the chemical solution deposition. The composition of 0.1 Zr-substitution tends to have a better crystallinity than 0.8 Zr. At annealing 800°C, the crystallite size for this BZT films is found around 118.99 nm. Sawyer-tower circuit measured the ferroelectric properties as hysteresis loops formed by our cluster-array data plotter. The crystallographic properties, c/a or tetragonality, of BaZr0.1Ti0.9O3 is noted to be 1.018 as the highest value which pre-assumed as good ferroelectric properties than other films. The plotted-hysteresis loops are well-identified as ferroelectric behavior.

The Sawyer tower circuit has been used to measureelectrical field and electrical polarization of material tested.The results of the measured-value show the maximum value of electric field which could be used as measurement parameter. The highest value of polarization, 34.12 $\mu C/cm^2$, have been determined and obtained on $BaZr_{0.1}T_{0.9}O_3$ at 800°C for 3 hours annealing process and its maximum electric field is noted to be about 38.3 Volt/cm on all samples.The crystallite size, which is affected by annealing, and the lattice parameter influence the ferroelectric properties in material.

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