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Crystallographic Properties of Aluminum-doped Barium Zirconium Titanate Thin Films by Sol Gel Process

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Abstract. We studied the crystallographic of Barium Zirconium Titanate thin films with Aluminum doped (BZAT). These films were prepared by sol-gel process and followed by spin coating. The sintering temperature is taken at 800°C and 900°C. We found that the crystallographic system of BZAT thin films have tetragonal structure with the lattice parameter slightly changed by various Aluminum partial substitution. When 0.01 Al moles added, the grain size of the films is 29.42 nm at 800°C. The sintering temperature 900°C increased the grain size into 50.95 nm. We also calculated the spontaneous polarization theoretically and we found the optimum value of BZT thin film with 0.01 mole Al heated at 800°C, is 0.143 C/m^2. This way, we could predict that the film has ferroelectric phase.

Introduction

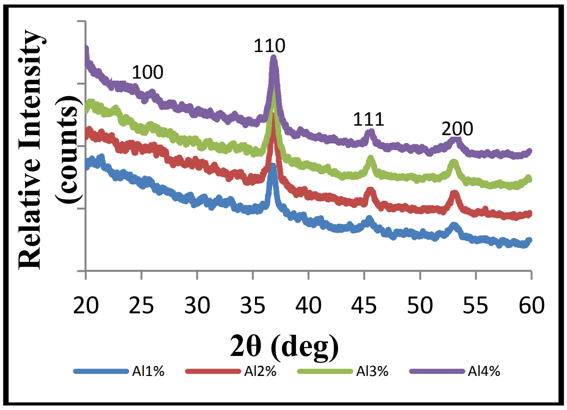
Lead-based perovskites materials are well known to have advantages for fabrication of performance devices such as solar cell [1]. However, there is so much concern for the environment, in this way Barium Zirconium Titanate become more interesting, since this material is lead-free. Utilizing base material $BaTiO_3$ which has unique properties, made Barium Titanate more usable when Zr added. Because of the ion Zr^{4+} more stable than Ti^{4+}, the substitution decreased effect of leakage current on films. When zirconium is added to $BaTiO_3$ systems it also decreases the grain size of the crystallized films [2]. Substitution other ion on ABO_3 perovskite structure is to change its system characteristics [3]. This is clearly explained that Barium Zirconium Titanate has a great potential to replace Barium Strontium Titanate as a tunable microwave device [4]. The advantages properties of BZT have a higher dielectric constant, high tunability, low dielectric loss, and lower leakage current [5]. Besides, a good ion stability made across the possibility for the application as memory and solar cell. BZT thin films itself had homogenous and dense microstructure with a smooth surface [6]. Another film that has advantages properties, aluminum oxide films have the inertness properties in chemical reaction, high resistivity, hardness, and abrasive. Aluminum oxide has a great resistant with respect to corrosion and high thermal conductivity. Aluminum oxide already used as hard coating and diffusion barrier to protect flat panel displays [7]. In this paper, we intend to study the crystallographic properties of aluminum atoms doped-$BaZr_{(0.1-x/2)}Ti_{(0.9-x/2)}Al_xO_3$ thin films to find the possibility of the application as solar cell.

Experimental Procedure

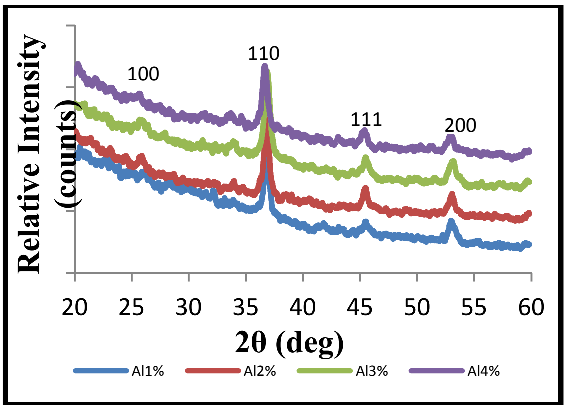
$BaZr_{(0.1-x/2)}Ti_{(0.9-x/2)}Al_xO_3$ (x ranging from 0.01 to 0.04 in the step of 0.01) 0.5 M 5mL are developed by Chemical Solution Deposition method and followed by spin coating on SiO_2 substrate. The cost-effective sol–gel process and spin coating in this study was described previously for other $BaTiO_3$ base material [8,9]. Barium acetate [$Ba(C_2H_3O_2)_2$] (99%), aluminum acetate [$C_4H_7AlO_5$], titanium isopropoxide[$Ti(OCH(CH_2)_2)_4$] (≥97%) from Sigma Aldrich and zzirconium n-butoxide[$C_{16}H_{36}O_4Zr$] (88%) from Alfa Aesar were used to synthesize BZAT solution. Stoichiometrically-calculated, barium acetate and aluminum acetate were dissolved in warm acetic acid[CH_3COOH](100%) from Merck KGaA Chemical by stirring. Finally, the Zr-Ti sol was added to Ba-Al solution at room temperature. To stabilize the BZAT solution, ethylene glycol[$C_2H_6O_2$] (≥99.5%) from Merck KGaA Chemical is also needed. The solution was deposited on SiO_2 substrate which is continued by spinning the substrates at 3000 rpm for 30 seconds [8]. To remove the remaining organic compounds and other undesired solution, the sample was treated by hydrolysis and pirolysis process about 5 minutes at 300°C. For the final step of BZAT ceramics, the sample is annealed at 800°C and 900°C about 3 hours with heating rate 10°C/menit to obtain the desired thin films. The characterizations of samples were examined by XRD Phillips Analytical PW371 to study the crystallographic properties. General Structure Analytical System (GSAS) program was used to find the lattice parameter accurately moreover to predict the spontaneous polarization by theoretical approach.

Result and Discussion

Crystallography Results. Fig. 1 showed the X-ray diffraction pattern for BZAT thin films in the range of $20^o \leq 2\theta \leq 60^o$ where all peaks are present. Using COD (Crystallography Open Database) material with entry no. 96-210-0861, perovskite tetragonal phase was observed for all aluminum doped composition in BZT films. There is no secondary phase identified from the X-ray diffraction pattern. As shown at X-ray diffraction pattern in Fig. 1, the growth of BZAT composition at 800°C better than the growth at 900°C. It showed BZAT has an optimum temperature at 800°C for the crystallization. Based on diffraction pattern, BZT with 0.02 mole of aluminum have the highest intensity rather than other moles. This is because the crystal structure reached the better crystallinity with respect to other samples. In case of Al moles increased, the crystal structure started damage.



(a)



(b)

Figure 1. X-ray diffraction patterns taken from $BaZr_{(0.1\text{-}x/2)}Ti_{(0.9\text{-}x/2)}Al_xO_3$ (x=0.01, 0.02, 0.03, and 0.04) thin films annealed at: (a) 800°C for 3 h and (b) 900°C for 3 h.

Table 1. Lattice parameter, tetragonality and spontaneous polarization of $BaZr_{(0.1\text{-}x/2)}Ti_{(0.9\text{-}x/2)}Al_xO_3$ (x=0.01, 0.02, 0.03, and 0.04) thin films at 800°C and 900°C

Sample Identification	mole Al	a (Å)	b (Å)	c (Å)	Tetragonality	Ps(C/m^2)
BZAT8001	0.01	4.0118	4.0118	4.0487	1.00919	0.143
BZAT8002	0.02	4.0026	4.0026	4.0353	1.00817	0.128
BZAT8003	0.03	4.0092	4.0092	4.0356	1.00657	0.102
BZAT8004	0.04	4.0040	4.0040	4.0334	1.00736	0.114
BZAT9001	0.01	4.0134	4.0134	4.0298	1.00410	0.064
BZAT9002	0.02	4.0144	4.0144	4.0345	1.00501	0.078
BZAT9003	0.03	4.0125	4.0125	4.0207	1.00203	0.032
BZAT9004	0.04	4.0263	4.0263	4.0540	1.00687	0.106

Using Rietveld refinement from GSAS program we estimated the lattice parameter of BZAT thin films, the values for each composition can be seen in Table 1. Method of Williamson-Hall was used to estimate grain size of the BZAT from lattice parameter [10]. Fig. 2 showed the value of grain size with the increasing of mole. For 0.01, 0.02 and 0.04 mole, the more temperature increased the more grain size grew. Exceptional for 0.03 mole, grain size at temperature 800^{o}C are found out as same as the grain size for 0.01 and 0.02 mole at 900^{o}C. This could happen possibly because the growth of grain size already reached saturation for 0.03 moles at 800^{o}C. Therefore when the temperature of BZAT 0.03 mole increased up to 900^{o}C, the grain size slightly decreased.

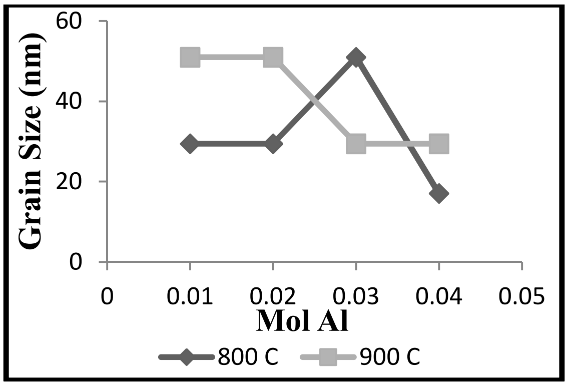


Figure 2. Grain size of $BaZr_{(0.1-x/2)}Ti_{(0.9-x/2)}Al_xO_3$ (x=0.01, 0.02, 0.03, and 0.04) thin films at 800^{o}C and 900^{o}C.

Ferroelectric phase can be characterized by knowing the asymmetry of the structure. The asymmetry of the structure has a relation with tetragonality. The tetragonality that are shown in Table 1 is the ratio between lattice parameter c and a. At 800^{o}C, tetragonality has decreased with the more Al added into BZT, but it increased when 0.04 Al mole added. In case of the temperature 900^{o}C, the highest tetragonality are found when 0.04 mole was added. Compared both the temperature, BZAT -0.01 Al mole added at 800^{o}C was found as the sample with the highest tetragonality. This value is higher than the tetragonality of BZT [11]. This is possible because partial substitution of Al itself tend to shift the position of ions which is depending on ion radii and ionic stability, but when the more probability of Al increased, the structure started to change and caused the tetragonality decreased, as well as by the effect of temperature.

Spontaneous Polarization. The ferroelectric phase is indicated by its spontaneous polarization. Table 1 shows the theoretical approach to find the spontaneous polarization. The theoretical approach is calculated by its lattice parameter [12]. To obtain the spontaneous polarization theoretically, we used the lattice parameter from GSAS software after partial substitution of Al added. The ionic displacement in perovskite structure also counted to the approach. The highest spontaneous polarization is 0.143 C/m^2 when the BZAT 0.01 mole was heated at 800^{o}C. Other side, we should have to pay more attention that the value didn't take contribution of electronic polarization of the ions. As we can see, the sample of 0.01 mole Al which is heated at 800^{o}C has the highest tetragonality and spontaneous polarization.

Summary

We have studied the crystallographic of the BZT with Al doped at the temperature 800^{o}C and 900^{o}C. It is found that BZT thin films were successfully doped by Aluminum. The X-ray intensity showed the optimum of doped Al was found for 0.02 Al moles and the temperature is 800^{o}C. The grain sizes of the samples also have unique value, especially for 0.03 Al moles, because more than 0.03 Al moles the crystal structure of BZAT slowly damaged. It is found when the sample was heated at 800^{o}C, BZAT 0.01 Al mole has a higher spontaneous polarization rather than other samples. BZAT thin film indicates the ferroelectric state. Therefore it can be used as solar cell devices.

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