

# HIGHLY PREFERRED ORIENTED LEAD BARIUM TITANATE THIN FILMS USING ACETYLACETONE AS CHELATING AGENT IN A SOL-GEL PROCESS

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**Abstract.** Ferroelectric  $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$  ( $\text{PB}_x\text{T}$ ) materials can be synthesized by a sol-gel process incorporating acetylacetone as a chelating agent to form ligand with titanium isopropoxide. It was found that a less cross-linking gel obtained at 120 °C and could be converted to nanometric-sized perovskite phase powder. A high purity of  $(\text{Pb}_{0.5}\text{Ba}_{0.5})\text{TiO}_3$  powder was obtained at 500 °C, with a nano-meteric size of about 30-50 nm the specific surface area of 21.91 m<sup>2</sup>/g. Furthermore, highly oriented  $\text{PB}_x\text{T}$  thin films were obtained by utilizing the as-prepared sol spin-coating on (100) MgO substrate. The oriented films were synthesized from all compositions between  $x = 0.2$  and  $x = 0.8$ , at a crystallization temperature of 600 °C. In particular, for the Ba content in the range of  $x = 0.5\sim 0.6$ , highly preferred (001)/(100) planes were observed.

## 1. INTRODUCTION

The solid solution system of lead barium titanate ( $\text{Pb}_{1-x}\text{Ba}_x\text{TiO}_3$ ,  $\text{PB}_x\text{T}$ ) is a perovskite ferroelectric, which has been recently reported as having extremely large electrostriction [1]. Therefore, it has been used to manufacture many electronic and optical devices by utilizing their excellent dielectric, piezoelectric and optical properties [2]. For electrostriction applications, the advantage of the anisotropic properties in these ferroelectric materials will be utilized, therefore, it is very important to prepare high-quality epitaxial (001) thin films [3].

The sol-gel process is a good route for powder/thin film preparation due to its low-temperature synthesis, easy-control of composition, and ability to produce fine structures [4]. The metal alkoxide can react easily with moisture to decrease the solubility of alkoxide in the solvent, so the preparation is

inconvenient [5]. However, acetylacetone is a known chelating agent with metal alkoxides since it significantly changes the hydrolysis behaviors during the sol-gel process, and leads to better ions homogeneity, enhances the powder's properties, and reduces the powder synthesis temperature [6].

Giridharan and Tayavel [7] have reported the characterizations of  $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{TiO}_3$  thin films via a sol-gel route by using acetic acid and 2-methoxyethanol as the chelating agent. More recently, acetylacetone as chelating agent, ethylene glycol as solvent, was identified for producing  $\text{Pb}_{1-x}\text{Ba}_x\text{TiO}_3$  precursor sols with good stability, and a highly oriented  $\text{PB}_x\text{T}$  thin film was successfully manufactured on MgO (100) substrate [8].

In this study, a mixed (001)/(100) highly preferred oriented  $\text{PB}_x\text{T}$  thin-films on MgO (100) substrates were prepared by the sol synthesized from the

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acetylacetone/ethylene glycol route by a sol-gel method. In addition, the effects of Ba content on the characteristics of the deposited oriented thin films were also examined.

## 2. EXPERIMENTAL PROCEDURE

Lead barium titanate powders were prepared with the chemical formula  $(\text{Pb}_{0.5}, \text{Ba}_{0.5})\text{TiO}_3$ . Barium acetate and lead acetate were dissolved in ethylene glycol, and a homogeneous Ba-Pb-acetate solution of 0.125M was prepared. Titanium isopropoxide was chelated with acetylacetone (molar ratio of acetylacetone/titanium isopropoxide at 4), to obtain a clear yellow-orange liquid. The resulting titanium compound was then dissolved into the acetylacetone/ethylene glycol solution under vigorous stirring. This solution, containing the cations according to the stoichiometry of  $(\text{Pb}_{0.5}, \text{Ba}_{0.5})\text{TiO}_3$  being Pb:Ba:Ti = 0.5:0.5:1.00, was refluxed at 60, 80, 120, and 140 °C, respectively, for 4 h. Hydrolysis and gelation were induced by the direction addition of water. The acetylacetone gel was obtained and dried in an oven. The dried gels were calcined at 500 °C for 4 h, and a white  $(\text{Pb}_{0.5}, \text{Ba}_{0.5})\text{TiO}_3$  powder was obtained.

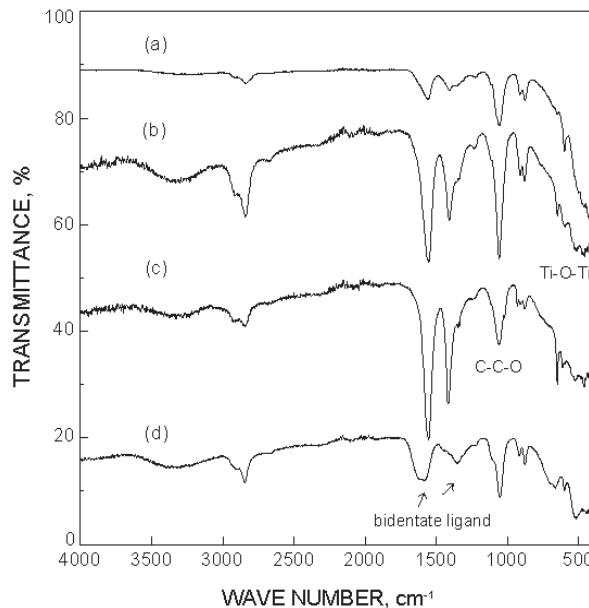
Various compositions of  $\text{PB}_x\text{T}$  sols obtained at 120 °C were spin-coated on substrate by using a spin coater at 4000 rpm for 30 sec for each coating. The as-deposited films were then pyrolyzed at 500 °C on a hot plate for 3 mins to evaporate residual organic species. The film was annealed at 600 °C for 2 h at a heating rate of 5 °C/min, and a cooling rate of 2 °C/min was applied to avoid the breaking of thin film.

The dried gels were investigated by Fourier transfer infrared spectroscopy (FTIR). Scanning electron microscope (SEM), X-ray powder diffraction (XRD), and Brunauer, Emmett and Teller (BET) specific surface area analyzer were utilized to analyze the calcined powders. Furthermore, the crystalline phase and orientation of the PBT film synthesized on MgO (100) substrates were examined by using XRD. The microstructures of films were observed by a SEM.

## 3. RESULTS AND DISCUSSION

### 3.1. Preparation of nanometric-sized $(\text{Pb}_{0.5}, \text{Ba}_{0.5})\text{TiO}_3$ powders

The FTIR spectra of the dried gel obtained from various gelation temperatures are shown in Fig. 1. The FTIR data indicate that there are two absorption bands at around 1560 and 1410 cm<sup>-1</sup> for all of the



**Fig. 1.** The FTIR spectra of Pb-Ba-Ti-gels obtained from various gelation temperatures. (a) gelated at 60 °C, (b) gelated at 80 °C, (c) gelated at 120 °C, and (d) gelated at 140 °C.

dried gels. These bands have been attributed to the asymmetric and symmetric C-O-Ti stretching vibration in acetylacetone chelating titanium alkoxide system [9]. However, the two peaks have also been observed in the sol-gel processing of acetate-containing systems and have been attributed to asymmetric and symmetric stretching modes of  $-\text{COO}^-$  [10]. Additionally, the absorption peak of C-C-O of ethylene glycol is about 1080 cm<sup>-1</sup> [11]. It has been reported that when the difference of these two absorption bands of asymmetric and symmetric vibrations ( $\Delta v$ ) is  $> 160$  cm<sup>-1</sup>, the acetate is a typical bridging bidentate ligand. When  $\Delta v$  is small than 80 cm<sup>-1</sup>, it is a chelating bidentate ligand.

In Fig. 1c, for the gel gelated at 120 °C, the FTIR spectrum shows the bidentate ligand difference to be 135 cm<sup>-1</sup>, which indicates that there is less bridging bidentate ligand. The starting material with a lower gelation temperature at 60 °C, has a bidentate ligand difference of 155 cm<sup>-1</sup>, larger than those in Figs. 1b and 1c. In addition, the dried gel gelated at 150 °C, showing the largest bidentate ligand difference 230 cm<sup>-1</sup> in Fig. 1d. This reveals that there is much crosslinking structure in the gel, leading to a need for higher temperature to break the Ti-O-C bonding. Therefore, the formation temperature of perovskite phase is higher than those of other cases.

A smaller bidentate ligand difference indicates a more highly chelated bidentate ligand, which leads to a lower rate of cross-linking and easier pyrolyzation of the Ti-O-C bonding. As a result, a lower formation temperature of perovskite phase as well as a finer powder can be expected. In contrast, the larger bidentate ligand difference reveals that the gel contained a great deal of crosslinking structure, it was relatively difficult to convert to a perovskite phase, and a bigger particle size was produced.

The powders examined by XRD were amorphous as calcined at temperatures below 400 °C (not shown). The precursor gels had started to crystallize via an intermediary phase at 450 °C, and at this temperature there is still some unreacted carbonate. At 600 °C the gel contained a higher amount of perovskite phase and fewer unreacted BaCO<sub>3</sub>, PbCO<sub>3</sub> and TiO<sub>2</sub>. Furthermore, there is only a small amount of BaCO<sub>3</sub>, and only a trace of TiO<sub>2</sub> observed as intermediate phases prior to the formation of (Pb<sub>0.5</sub>,Ba<sub>0.5</sub>)TiO<sub>3</sub> phase during the decomposition of the dried gel. Only traces of BaCO<sub>3</sub> and TiO<sub>2</sub> remaining should be considered as an almost perfect mixing of the constituent cations in the gels. This can indicate that the perovskite phase is obtained from the amorphous powder precursor without significant segregation of the individual metals directly.

The (Pb<sub>0.5</sub>,Ba<sub>0.5</sub>)TiO<sub>3</sub> powders prepared from various gelation temperatures were examined by SEM, BET specific surface area analyzer and laser particle size distribution analyzer, respectively; and are listed in Table 1. The specific surface area of the powder obtained from gelated at 120 °C is 21.92 m<sup>2</sup>/g and the particle size of the nanometric sized powder is 30-50 nm. Table 1 shows that the mean particle size of powders obtained by SEM ( $D_{SEM}$ ) is smaller than that obtained by the laser particle size distribution analyzer ( $D_{LPD}$ ) for the calcined perovskite powders.

The primary particle sizes are small but aggregated, revealed by the examination of SEM and  $D_{LPD}/D_{SEM}$ , having primary particle sizes of 60-90 nm,

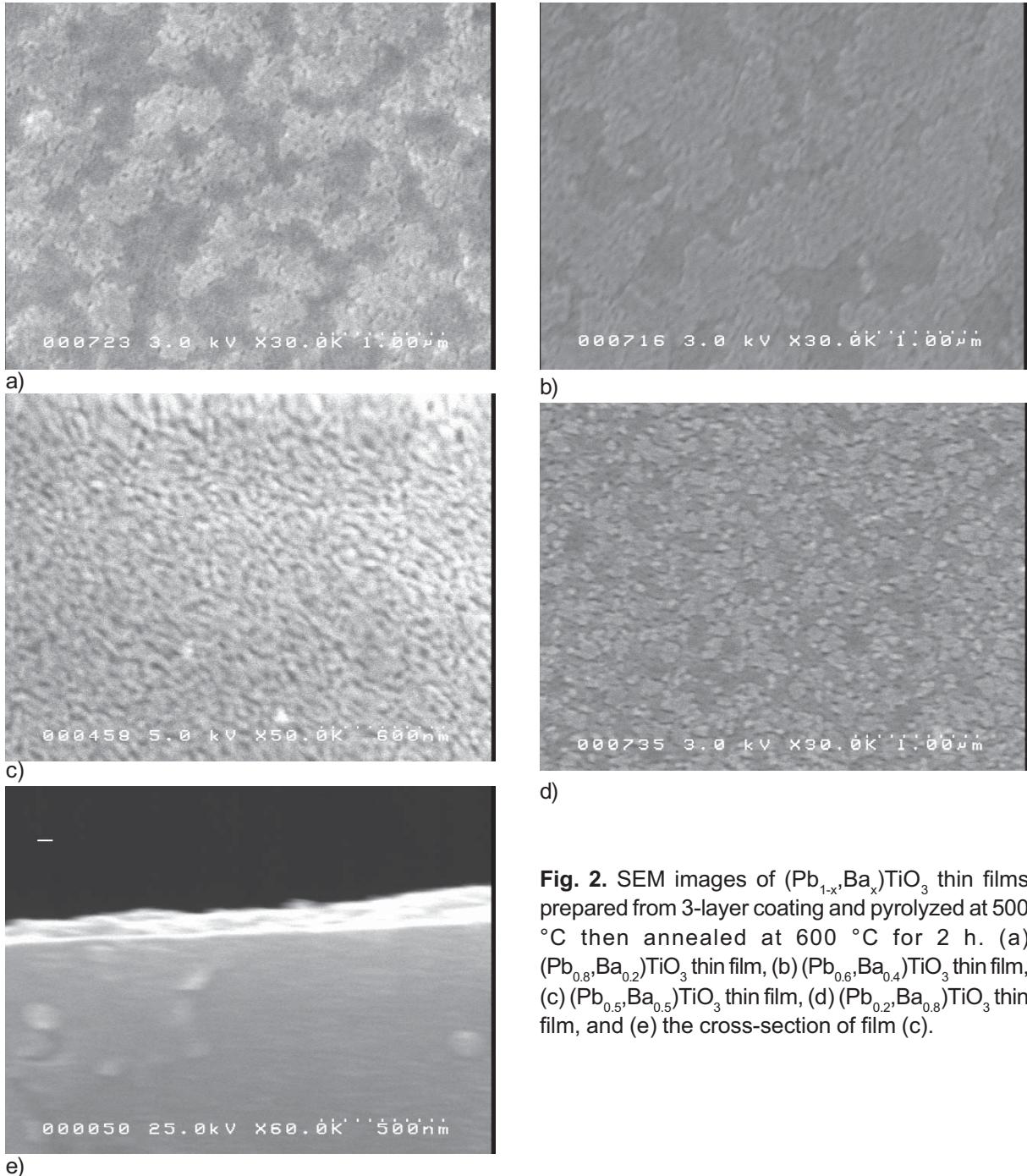
40-60 nm and 30-50 nm for powders obtained at various gelation temperatures of 60, 80, and 120 °C, respectively. This result confirms that the powders prepared by the acetylacetone/ethylene glycol sol-gel method in the present work are perovskite phase materials of nanometer size. This study shows that the morphologies of the formed powders are dependent on the gelation temperature during the sol-gel process. The obtained (Pb<sub>0.5</sub>,Ba<sub>0.5</sub>)TiO<sub>3</sub> powder is fine in particle size as the gelation temperature increased up to 120 °C. The particle size of the gel obtained at 120 °C is smaller and the particle size of the powder calcined from the gel is also very fine. The FTIR spectra of the dried gel prepared at various gelation temperatures (shown in Fig. 1) shows that the gel obtained from a higher temperature demonstrating smaller  $\Delta v$  has a lower rate of cross-linking and a smaller particle size of precursor gel. This higher gelation temperature makes it easier to have a more chelating coordination. Hence, the particle size of powder obtained from the calcination of a less crosslinking gel also contains smaller particle size. On the other hand, the lower gelation temperature makes a more bridging bidentate coordination. When there are more bridging structures, a higher rate of cross-linking of the gel, and a bigger particle size of gel makes the gel calcined to a bigger particle size of (Pb<sub>0.5</sub>,Ba<sub>0.5</sub>)TiO<sub>3</sub> powder.

### 3.2. (001)/(100) preferred oriented PB<sub>x</sub>T thin films

By using a minimum amount of ethylene glycol as the modified solvent to dissolve lead acetate and barium acetate, the PB<sub>x</sub>T sols can be prepared without any detectable precipitation after stock at room temperature for 12 months. The processing temperature used in this study was 150 °C higher than the crystallization temperature, 450 °C, obtained from the powder studies. Thus, the annealing temperature of PB<sub>x</sub>T thin film was 600 °C.

**Table 1.** The powder properties of nanometric-sized (Pb<sub>0.5</sub>,Ba<sub>0.5</sub>)TiO<sub>3</sub> powders prepared from various gelation temperatures and calcined at 500 °C.

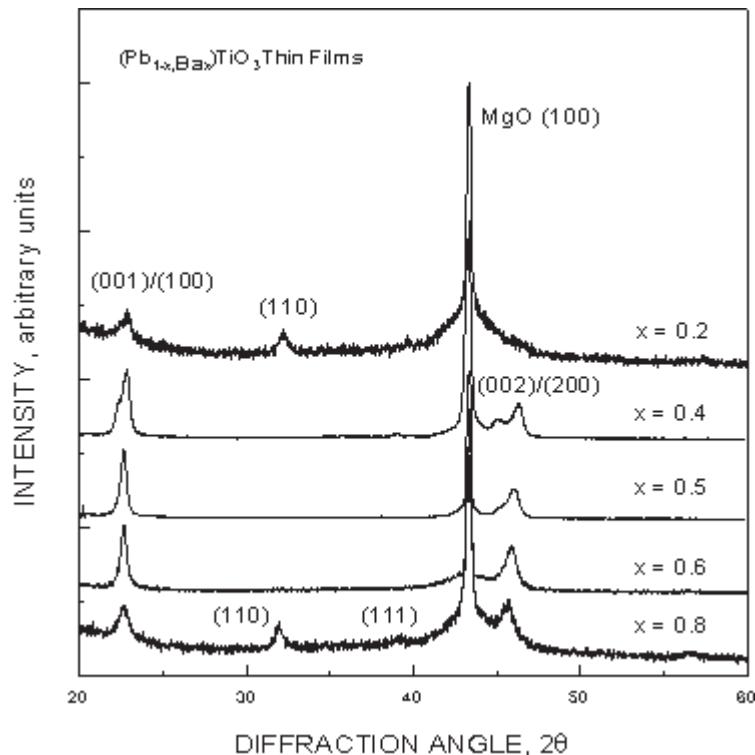
	$D_{SEM}$ (nm)	$S_{BET}$ (m <sup>2</sup> /g)	$D_{LPD}$ (nm)	$D_{LPD}/D_{SEM}$
60 °C	60-90 (75±15)	14.54	376	5,01
80 °C	40-60 (50±10)	20.71	230	4,60
120 °C	30-50 (40±10)	21.91	138	3,45



**Fig. 2.** SEM images of  $(\text{Pb}_{1-x},\text{Ba}_x)\text{TiO}_3$  thin films prepared from 3-layer coating and pyrolyzed at 500 °C then annealed at 600 °C for 2 h. (a)  $(\text{Pb}_{0.8},\text{Ba}_{0.2})\text{TiO}_3$  thin film, (b)  $(\text{Pb}_{0.6},\text{Ba}_{0.4})\text{TiO}_3$  thin film, (c)  $(\text{Pb}_{0.5},\text{Ba}_{0.5})\text{TiO}_3$  thin film, (d)  $(\text{Pb}_{0.2},\text{Ba}_{0.8})\text{TiO}_3$  thin film, and (e) the cross-section of film (c).

The morphologies of  $\text{Pb}_{1-x}\text{Ba}_x\text{TiO}_3$  films were examined by SEM. It revealed that the surfaces of the films were crack-free in evidence of the usage of acetylacetone/ethylene glycol that can prevent the crack of thin films. The SEM surface images of the 3-layer coating  $\text{Pb}_{1-x}\text{Ba}_x\text{TiO}_3$  films pyrolyzed at 500 °C and annealed at 600 °C for 2 h are shown in Fig. 2. As seen in Figs. 2a, 2b, and 2d, the morphologies of the  $\text{PB}_x\text{T}$  at  $x=0.2, 0.4$ , and  $0.8$ , respectively, show less-textured structures containing of two different grains, and a significant porosity also

examined (Figs. 2a & 2d). However, the less-textured porous films leading to less orientation were examined by XRD as shown in Fig. 3. The results were in good agreement with the studies of Liu [12]. The microstructure of  $(\text{Pb}_{0.5},\text{Ba}_{0.5})\text{TiO}_3$  film exhibits more homogeneous and densified grains of about 40-60 nm as shown in Fig. 2c. The textured densified films causing highly preferred oriented films examined by XRD will be shown in Fig. 3. Furthermore, cross-section of all  $\text{PB}_x\text{T}$  film layers revealed a microstructure through the film thickness of about



**Fig. 3.** XRD patterns of  $(\text{Pb}_{1-x}, \text{Ba}_x)\text{TiO}_3$  films prepared from 3-layer coating and pyrolyzed at  $500^\circ\text{C}$  then annealed at  $600^\circ\text{C}$ .

200 nm. The fractured surface of the  $(\text{Pb}_{0.5}, \text{Ba}_{0.5})\text{TiO}_3$  film is illustrated in Fig. 2e as an example.

The XRD patterns of the  $\text{PB}_x\text{T}$  films (3 layers coating) containing different Ba contents fabricated on MgO (100) substrates, and pyrolyzed at  $500^\circ\text{C}$ , are shown in Fig. 3. For the films on MgO substrates, (001)/(100) and (002)/(200) peaks are observed. There is a relatively higher purity of (001)/(100) peak detected when the Ba content is  $0.5 \sim 0.6$ , as well as a narrow full width at half maximum (FWHM) of (001)/(100). In contrast, as the Ba is increased to  $x = 0.8$ , the (100) peak becomes broad again accompanied by a number of other planes. It could be explained that the Ba compositions in the film is increased, the tetragonal perovskite phase of the  $\text{PB}_x\text{T}$  films has been changed to cubic structure [13]. Thus, the main peaks of (001) and (100) are merged with increasing Ba content in the film. A narrow FWHM (001)/(100) peak without other planes is observed on films prepared from Ba content of 0.5-0.6.

Noticeably, the  $\text{BaTiO}_3$  sol spin coated on MgO (100) revealed that it was hard to get a preferred oriented (100) thin film. It is suggested that the

$(\text{Pb}_{0.2}, \text{Ba}_{0.8})\text{TiO}_3$  film contains much Ba to exhibit a structure close to cubic  $\text{BaTiO}_3$ , the lattice constant of  $\text{BaTiO}_3$  is mismatched with MgO, thus, a broad (001)/(100) peak with a few other planes is observed.

#### 4. CONCLUSIONS

$(\text{Pb}_{0.5}, \text{Ba}_{0.5})\text{TiO}_3$  nanometric-sized powders and thin films can be obtained from acetylacetone/ethylene glycol by a sol-gel process. FTIR, SEM and XRD were utilized to investigate the effects of gelation temperature on the formation and properties of the perovskite powders. At a higher gelation temperature ( $120^\circ\text{C}$ ), a less bridging bidentate ligand was obtained and led to a less cross-linking gel. The less cross-linking gel can be converted to perovskite phase at temperatures as low as  $450^\circ\text{C}$ , exhibited a nanometric size of about 30-50 nm and the specific surface area was  $21.91 \text{ m}^2/\text{g}$  at calcining temperature of  $500^\circ\text{C}$ .

The surfaces of the  $\text{PB}_x\text{T}$  films were crack-free in evidence of the usage of acetylacetone/ethylene glycol that can prevent the crack of thin films. However, the film thickness was about 200 nm obtained

from examining the cross-section of film layers by SEM. In addition, the (001)/(100) oriented films were synthesized from all compositions between  $x = 0.2$  and  $x = 0.8$ , at the crystallization temperatures of 600 °C. In particular, with the Ba content of  $x=0.5\sim0.6$ , highly preferred (001)/(100) planes accompanying by homogeneous and densified grains of textured films were observed.

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