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# INVESTIGATION ON STRUCTURAL AND FERROELECTRIC PROPERTIES OF $Bi_{3.25}La_{0.75}Ti_3O_{12}$ THIN FILMS

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## ABSTRACT

Lanthanum doped bismuth titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$ abbreviated as BLT) has been known as one of typical materials for Bi-layered perovskite structure which possess several unique properties such as good fatigue with metal electrode and stable remanent polarization, hence it has potential applications in ferroelectric random access memory. In this work, the BLT thin films were fabricated on $Pt/TiO_2/SiO_2/Si$ substrates by using a solution process, and then their features including crystal structure, surface morphology, and electrical properties were characterized by using X-ray diffraction system (XRD), scanning electron microscopy (SEM), and electrical measurement system (Radiant Precision LC 10), respectively. The obtained results point out that the BLT thin film annealed at 725 °C is mostly optimum from a viewpoint of film quality and ferroelectricity. In particular, the optimum BLT thin film having a thickness of 200 nm does not contain any cracks on the sample surface, and the grain size is closed to 400 nm from SEM observation. XRD patterns imply that the BLT thin film had stoichiometric structure with preferred orientations of (117) and (006), when annealed at temperatures higher than 725 °C. In addition, we found the influence of La (0.75) dopping on *c*-axis-oriented growth of BLT thin films is clear from the structural analysis. The remanent polarization of optimum BLT thin film is approximately 10 $\mu C/cm^2$, but the ferroelectric hysteresis loops are not saturated at low applied voltages.

*Keywords:* BLT, perovskite, ferroelectric, memory, thin film.

## 1. INTRODUCTION

In recent years, ferroelectric thin films have extensively attracted attentions in the world because of its abundant applications in MEMS sensor devices, ferroelectric random access memory (FeRAM), or 3D high-density capacitor [1, 2]. Among ferroelectric materials, $Pb(Zr_xTi_{1-x})O_3$, named as PZT, is known as one of the most important options owing to dominant advantages such as low crystallization temperature and high remanent polarization. Unfortunately, the chemical components in PZT are seriously harmful to the environment, or the poor fatigue of PZT leads to limit the utilization of metal electrodes like Pt, Au, or Al. Despite the fatigue of metal/PZT/metal capacitor is poor, it could be significantly improved by using metal oxide electrodes such as $RuO_2$, $IrO_2$, and $LaNiO_3$. It has been reported that the issue of these electrodes is normally to require complicated fabrication process, and it tends to increase leakage current [3]. Therefore, it is necessary to develop ferroelectric materials for improving the poor fatigue when using pure metal electrodes. Hitherto, typical ferroelectric materials such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BIT) are particularly considered to replace PZT. Although the fatigue of SBT reached $10^{12}$ cycles when switching the polarization continuously, the disadvantages of SBT are high crystallization temperature (750 – 825 °C) and small remanent polarization ($2P_r = 4 \div 16\ \mu C/cm^2$) [4, 5]. On the other hand, for the single crystal BIT material, the spontaneous polarizations ($P_s$) in *a*-axis and *c*-axis are 50 $\mu C/cm^2$ and 4 $\mu C/cm^2$, respectively, but the single crystals require expensive and complicated technique in principle. For the polycrystalline BIT thin film, the remanent polarization ($2P_r$) is as small as $4 \div 8\ \mu C/cm^2$ and the leakage current is high, leading to be difficult to apply BIT for the practical devices [6]. A recent research has released that $Bi^{3+}$ ion in $Bi_4Ti_3O_{12}$ structure could be substituted by valence ions in group III (for example, Lanthanum) to enhance the ferroelectric properties, especially the fatigue [7]. In this work, we have carried out the fabrication of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films via using a solution process, because it is simple, low-material and low-energy consumption compared with the other techniques. In sequence, the investigation on crystal structure, surface morphology, and electrical properties is systematically performed to find out the optimum condition for the BLT thin films.

## 2. EXPERIMENTAL PROCEDURES

The BLT thin films were fabricated on $Pt/TiO_2/SiO_2/Si$ substrates. In the sample structure, $SiO_2$ plays a role to isolate the gate electrodes when patterned, $TiO_2$ layer is deposited to enhance the adhesion of Pt thin film on $SiO_2/Si$ substrate, and Pt layer is a bottom-gate electrode. To prepare thin films, first, $Bi_{3.25}La_{0.85}Ti_3O_{12}$ solution precursor was uniformly dropped on the surface of $Pt/TiO_2/SiO_2/Si$ substrates, which were precleaned in acetone solvent and deionized (DI) water by using ultracleaner. Second, the samples covered with the BLT precursor were rotated with a buffer speed of 500 rpm in 10 seconds and a stable speed of 2000 rpm in 40 seconds to ensure the film uniformity. Third, the samples were, in turn, dried on a hot plate at 150 °C for 1 minute and 250 °C for 4 minutes to break steadily bonds and change the thin film from the solution state to the amorphous state. The spin-coating process was repeated 4 times to prepare the desired thickness of about 200 nm for BLT thin films, according to the cross-sectional SEM observation. Finally, the thin films were annealed to change from the amorphous state to the crystalline state at various temperatures 650, 675, 700, 725, 750, 775, 800 and 825 °C, by using a rapid thermal annealing system (model GSL1600X) for 15 minutes in oxygen atmosphere to supply reactive gases enough in crystallization mechanism. The surface morphology and the crystal structure of the fabricated BLT thin films were investigated by using scanning electron microscopy (NOVA NANOSEM 450) and using X-ray diffraction system (model D5005), respectively. To evaluate electrical properties, Pt thin film electrodes in dot form, whose diameter are 100, 200, and 500 $\mu m$, were deposited on the ferroelectric BLT thin films, by sputtering system (BOC Edward FL500). The ferroelectric hysteresis loops (*P-E*) and the leakage current characteristics (*I-t*) were characterized by using radiant precision LC 10 system.

## 3. RESULTS AND DISCUSSION

### 3.1. Crystal structure

Figure 1 shows XRD patterns of the BLT thin films fabricated at various temperatures. It is obvious that the intensity of diffraction peaks has changed significantly when rising the annealing temperature. At the annealing temperature of 650 °C, it begins to appear the Bi-layered perovskite structure from the diffractive planes such as (117), (200), and (220). However, the spectral peaks are quite wide and not sharp, that is, the crystallization of BLT thin films is not completed, or just likes the microcrystalline state. When the annealing temperature is continued to increase, for example at 675 and 700 °C, the crystallization are almost unchanged, but further increment to 725 °C, the XRD spectra appear clear picks at the diffractive planes of (004), (006), and (117). Taking a comparison with a recent research reported by Kang *et al.*, the typical peaks of stoichiometric structure of BLT thin films were only started at 750 °C, according to their XRD results [8]. It means that the crystallization temperature of BLT thin film is 25 °C lower in our work, which is favorable from a point of view on better technology. Moreover, we observe that the pick intensity becomes higher when increasing annealing temperature up to 825 °C, especially there is a dramatic change at [004], [006], and [008] peak positions. This result can be explained because the prior orientation of Bi-layered perovskite structure is *c*-axis, i.e. (*00l*) plane is more preferred than others, the molecular density of BLT is the highest in [*00l*] direction, leading to the lowest energy in (*00l*) plane.

To analyze on crystallization process in more details, the XRD patterns of the optimum BLT thin film annealed 725 °C was separately plotted as shown in Fig. 2. One can see that the diffraction peaks illustrate clearly the sharpness and the high-level crystallization, and it is congruous for the fabrication of $Pt/BLT/Pt/TiO_2/SiO_2/Si$ ferroelectric capacitor because if the annealing temperature is high over, the layers on Si substrates can be peeled off, and the process expends much energy and long time as well.

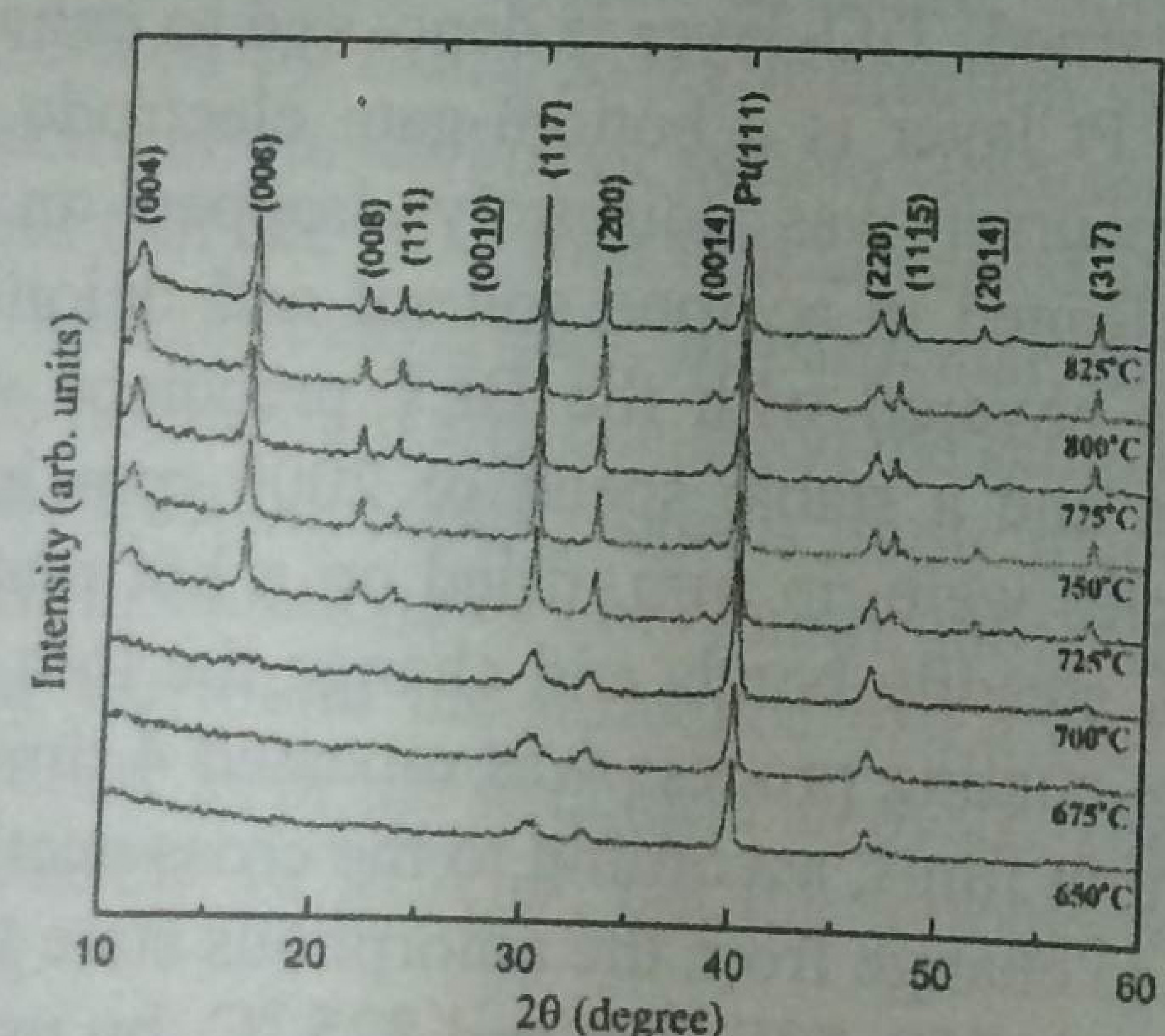


*Figure 1.* X-ray diffraction patterns of BLT thin films annealed at various temperatures.

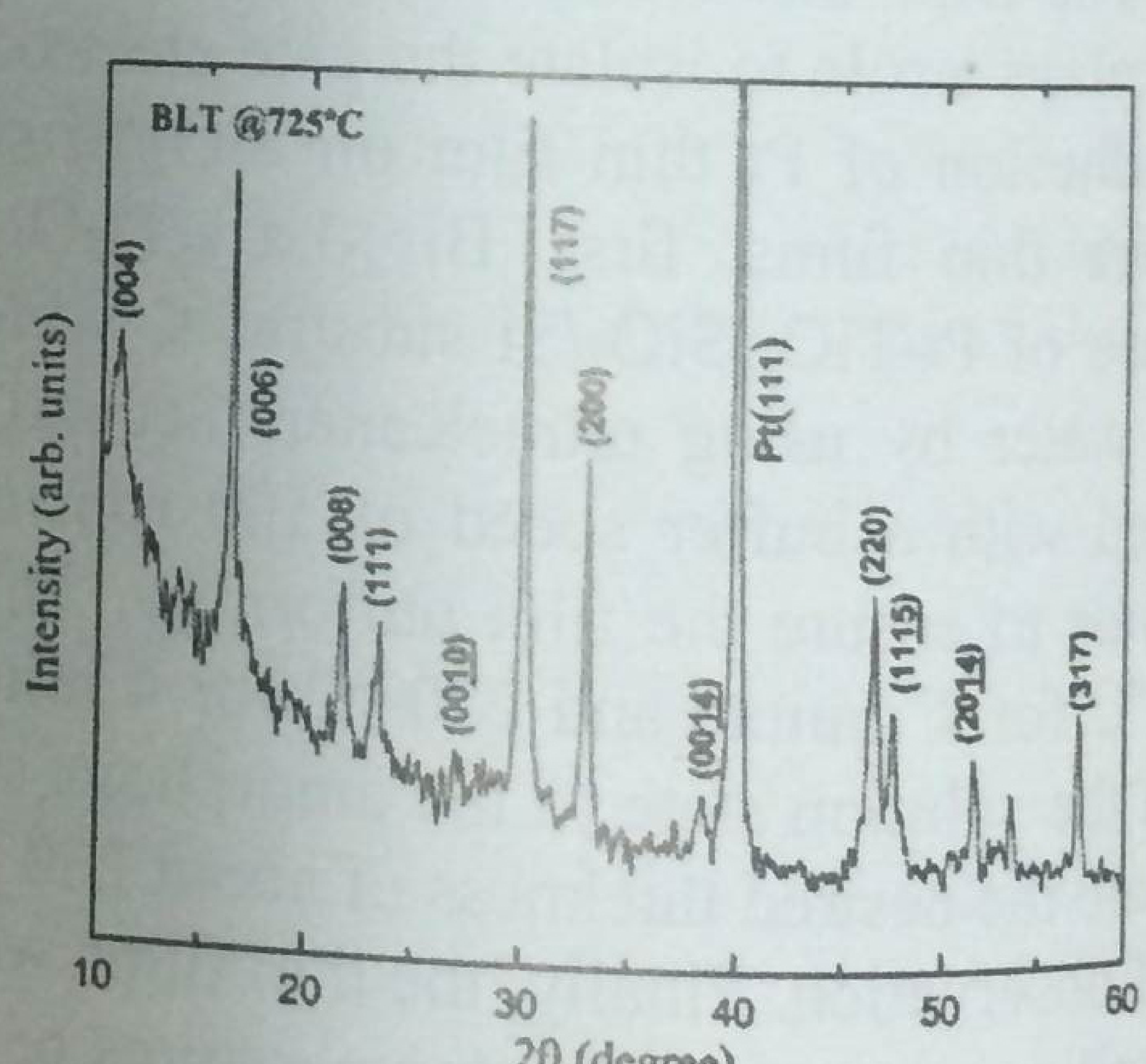


*Figure 2.* X-ray diffraction pattern of the BLT thin film annealed at 725 °C.

### 3.2. Surface morphology

The surface morphology of BLT thin films annealed from 650 °C to 825 °C is shown in Fig. 3. SEM images provide that the BLT thin films are uniform, smooth, and non-cracked. It means that the fabrication technology is suitable for high-quality BLT thin films using a solution process, instead of conventional vacuum technology.

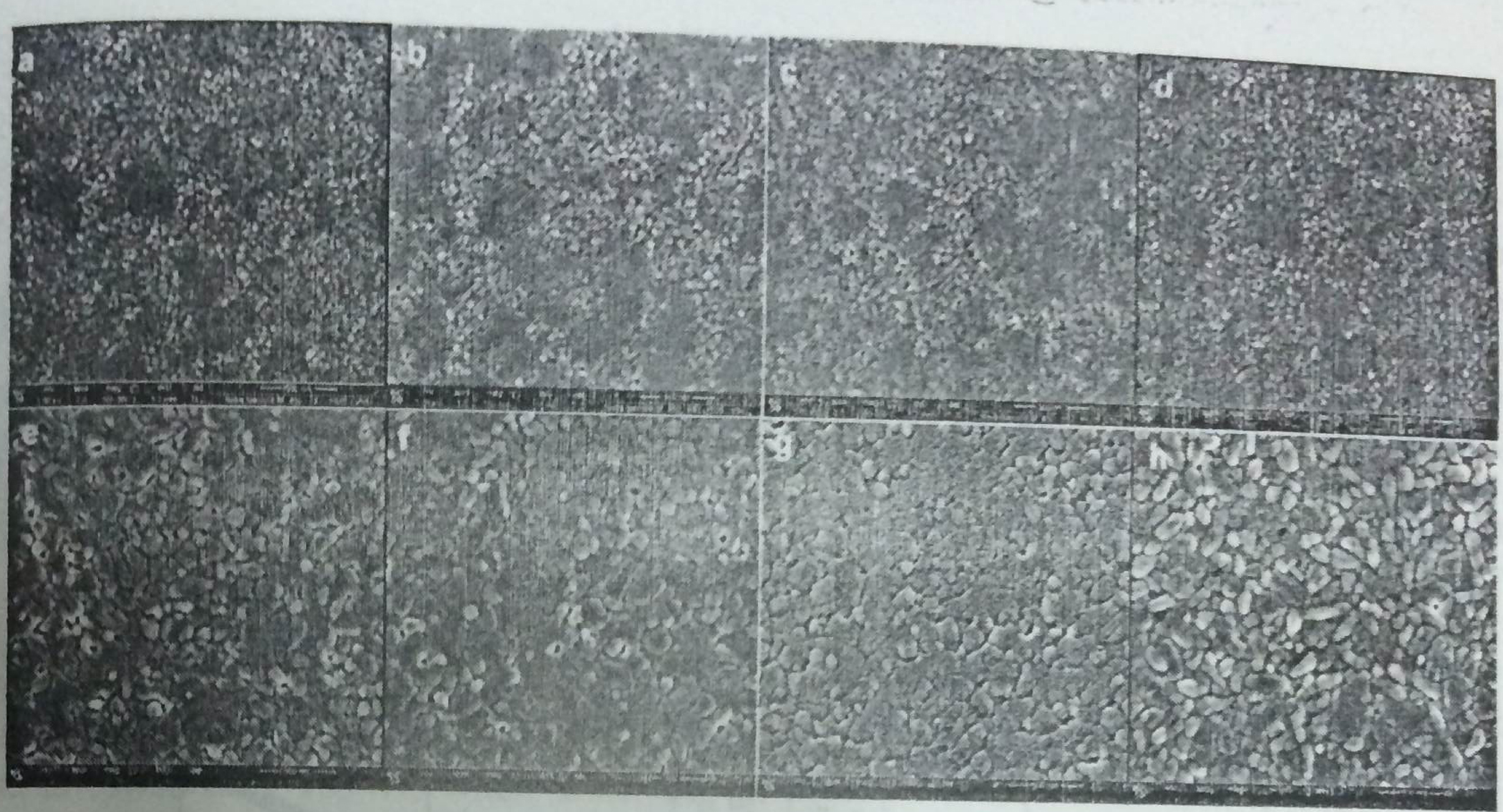


*Figure 3.* Surface morphology of the BLT thin films annealed at: a) 650 °C, b) 675 °C, c) 700 °C, d) 725 °C, e) 750 °C, f) 775 °C, g) 800 °C and h) 825 °C.

From Fig. 3, we observe that when increasing temperature, the grain size rises steadily, for example, when the temperature increased from 650 °C to 725 °C, the grain size expands slightly and the porous density decreases gradually. The grain size of the BLT thin film annealed at 650 °C is about 30÷50 nm, and that of BLT thin film annealed at 725 °C is about 100 nm. In addition, for the BLT thin films annealed at higher than 750 °C, the grain size is larger than that annealed at 725 °C, however, the grain distribution is not highly uniform, and it appears a lot of oval shapes, though the porous density falls down dramatically. Figure 3(h) is a typical surface image of BLT thin film annealed at 825 °C. We can see that when rising the annealing temperatures from 750 to 825 °C, the grain size increases slightly to 400 nm and the porous density decreases obviously as mentioned above. That is, the crystallization level is totally resembled with the XRD results obtained from Fig. 1. Comparing to the grain size of non-doped BIT thin film annealed at 700 °C reported as large as 2000 nm, which might be a drawback of polycrystallize thin films [9, 10], it is evidential that $La^{3+}$ ion plays a role as an important factor to stop the grain growth in the BIT thin films, in our research.

### 3.3. Ferroelectric hysteresis loops

Figure 4 represents the *P-E* loops of BLT thin films annealed at 650 °C and 675 °C. One can be seen that the polarization is linear dependence of the electric field, that is, the *P-E* loops are narrow and like straight lines. In these cases, the polarization is back to 0 when the electric field is swiched off, which is a nature of paraelectric materials. It seems to be reasonable with the results shown in Fig. 1, where the crystal structure of BLT thin films is amophous or microcrystal, but not stoichiometric as expected.

Figure 5 shows the *P-E* loops of BLT thin films annealed at 700 °C and 725 °C. From this figure, we can realize that the *P-E* loops are expanded comparing with the lower temperature cases of Fig. 4, and the *P-E* loops are tended to a typical hysteresis of ferroelectric materials, for instance, the sample annealed at 700 °C. When rising annealing temperature to 725 °C, the *P-E* loops of the BLT thin film exhibit obviously ferroelectric properties, which are symmetrical, but do not reach an adequate saturation. Based on Fig. 5 (b) for the BLT thin films annealed at

725 °C, at the applied voltage of 5 V, the remanent polarization ($P_r$) can be extracted to be 10 $\mu C/cm^2$, which is matching with the other reports [11 - 13]. This value is quite small, compared to the value $P_r = 41$ $\mu C/cm^2$ reported by Tomar *et al.* [14]. In our paper, although we do not present the results of BLT thin films annealing at temperatures higher than 725 °C, *P-E* hysteresis loops show the breakdown behavior of insulating materials, corresponding to the leakage current are overloaded. This problem is tentatively assumed because the thickness and the surface morphology of BLT thin films fabricated are not uniform overall, and the thinnest film area are easily breakdown due to the giant electric field at the local region, or the tunnel effect from the grain boundary, which would be discussed in the next section. In consequence, we conclude that the *P-E* loops completely resembles with results from XRD patterns and surface morphology of BLT thin films annealed at 725 °C as seen from Fig. 2 and Fig. 3.

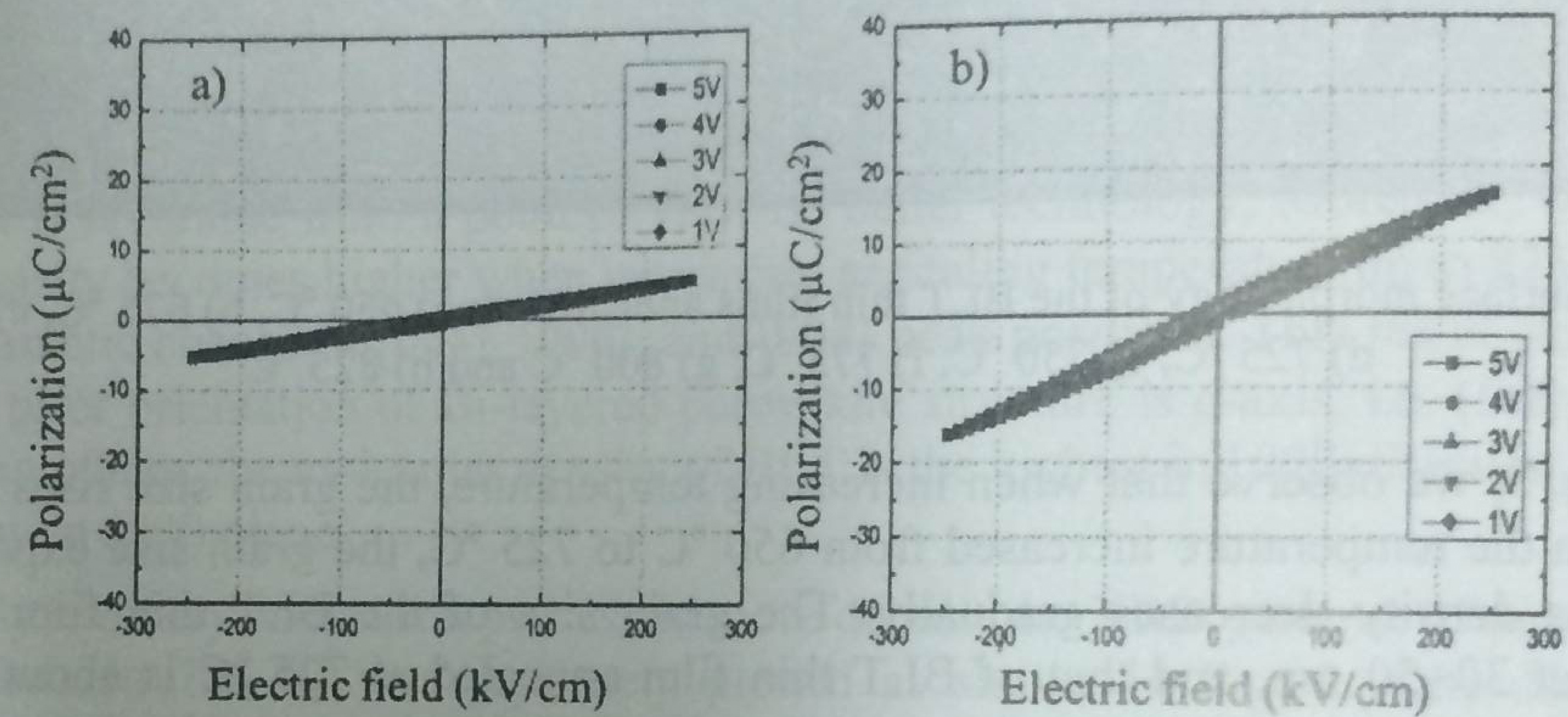


*Figure 4.* Ferroelectric hysteresis loops of BLT thin films annealed at: a) 650 °C, and b) 675 °C.

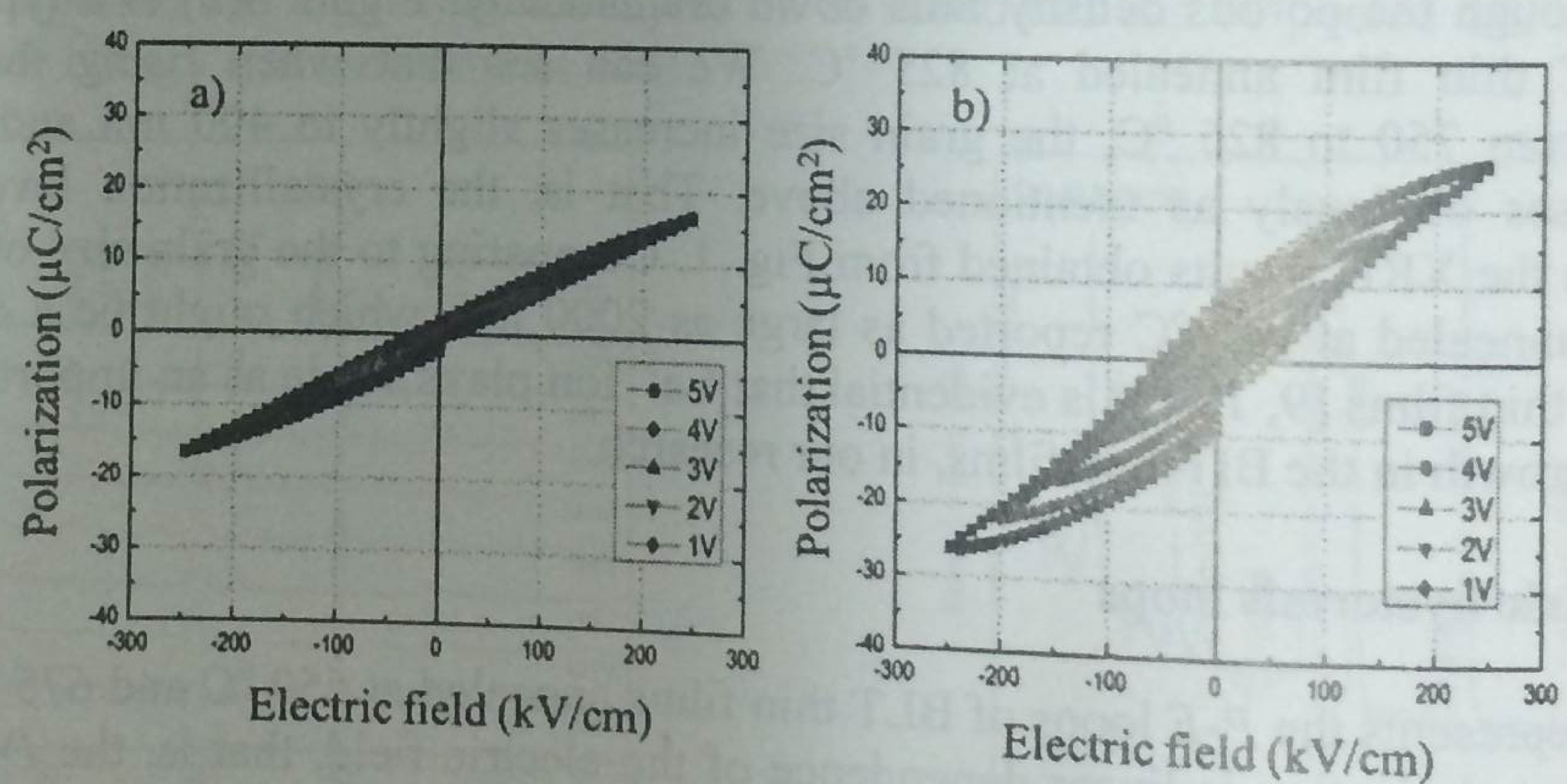


*Figure 5.* Ferroelectric hysteresis loops of BLT thin films annealed at: a) 700 °C, and b) 725 °C.

### 3.4 Leakage current characteristics

As for ferroelectric insulator materials, the investigation on the leakage current characteristics (*I-t*) when the voltage applied is essential to evaluate the insulating quality. Generally, the leakage current characteristics are divided into three regions, which depend on the amplitude of voltages. The first region is a linear dependence on voltage, and follows Ohm's law. The second one is known as the contribution of discharge current, proposed by Pool – Frankel and Schottky. The third one relates to the insulator-breakdown effect or the Fowler – Nordheim tunneling effect. Importantly, the leakage current characteristics provide the energy consumption of the electrionic device when stand-by status or not in use. Therefore, apart from the investigation on the *P-E* loops, the *I-t* characteristics of BLT thin film annealed at different temperatures were measured for each polarization voltage, as shown in Fig. 6. We observe that the leakage current of BLT thin films is lower than $10^{-4}$ A, when annealing at temperatures lower than 725 °C, and it is almost the same with the other samples annealed at 650, 675 and 700 °C. For the BLT thin films annealed at temperatures higher than 725 °C, the *I-t* appears the breakdown phenomenon between top and bottom electrodes. This is evidenced for consideration on the grain size rising with the annealing temperature as shown in Fig.3, which makes the discharge effect through the grain boundaries more strongly, and leads to easy breakdown of the insulating film layer.

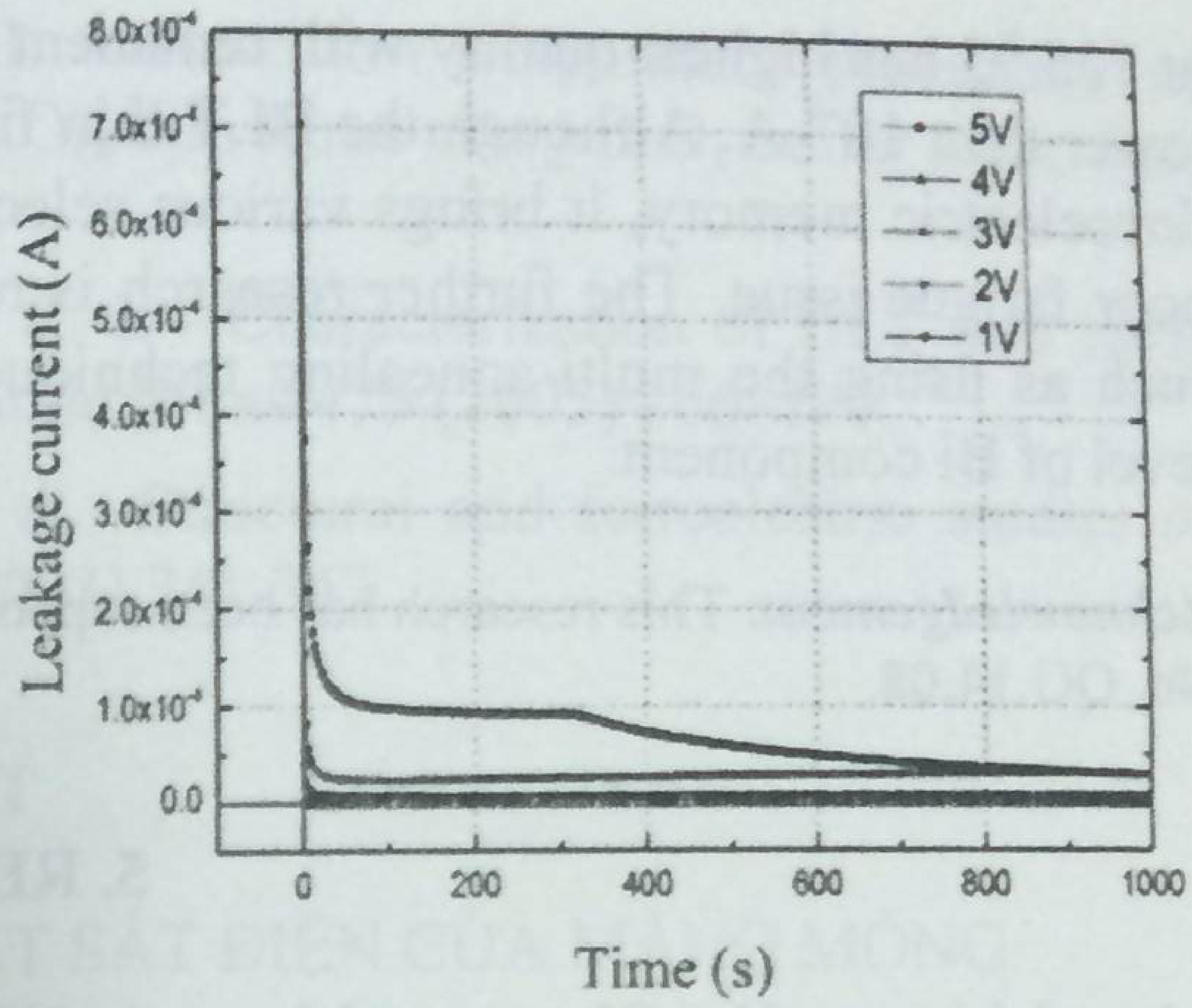


*Figure 6.* Leakage current characteristics (*I-t*) of the BLT thin film annealed at 725°C.

From *I-t* characteristics, we point out that even at $t = 0$, the leakage current is quite high for each applied voltage, critically for the cases of 4 and 5 V. This is because the equiqment does not remove the remanent polarization of ferroelectric material before each measurement. The remanent polarization is alike a minor power source which contributes the high leakage current at $t = 0$, *i.e.* even at zero voltage as shown in Fig. 6. Furthermore, in the case of 5 V, the *I-t* shape is not as smooth as others. The abnormal peak is contributed from the polarization current of ferroelectric material, which appears in the *I-t* measurement for the applied voltage of 4 V. Both the high leakage current phenomenon at $t = 0$ and the rugged shape of *I-t* characteristics are able to neglect when using a techique which decreases steadily the applied voltage to 0, like a sine pulse, in order to neutralize remanent polarization before measuring the *I-t* in each applied voltage. Therefore, one can conclude that the BLT thin film annealed at 725 °C has the best hysteresis loops, but not possible to compare with the traditional PZT material. In other words, the quality of ferroelectric BLT thin films must be further optimized to approach the practice in use for ferroelectric memory or other electronic devices.

## 4. CONCLUSION

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) ferroelectric thin films with the thickness of about 200 nm have been successfully fabricated on $Pt/TiO_2/SiO_2/Si$ substrates by using a solution process. X-ray diffraction results show that BLT thin films had stoichiometric Bi-layered perovskite structure with main (117) and (006) orientations at high temperatures ≥ 725 °C. SEM images describe that the BLT thin films fabricated have not cracked on the surface, the grains grow steadily in size, and the porous density reduces gradually with the increase of annealing temperature. One observes that the grain size of BLT thin film annealed at 650 °C is about 30 - 50 nm, and that in BLT thin film annealed at 725 °C is about 100 nm. We obtained that the BLT thin film annealed at 725 °C has highest quality with remanent polarization of about 10 $\mu C/cm^2$ and leakage current lower than $10^{-4}$ A. Although the BLT thin film fabricated has not suitably supported to apply for ferroelectric memory, it brings various selections of ferroelectric materials, aiming to reduce the poor fatigue issue. The further research is required to improve the properties of BLT thin films such as using the multi-annealing technique to crystallize each layer or changing the dopping level of Bi component.

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## TÓM TẮT

## NGHIÊN CỨU CẤU TRÚC VÀ TÍNH CHẤT SẮT ĐIỆN CỦA MÀNG MỎNG $Bi_{3.25}La_{0.75}Ti_3O_{12}$

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Vật liệu Bismuth Titanate pha tạp Lanthanum ($Bi_{3.25}La_{0.75}Ti_3O_{12}$; viết tắt là BLT) được biết đến là vật liệu tiêu biểu cho cấu trúc perovskite kẹp lớp Bi và cho thấy nhiều tính chất nổi trội như quá trình già hóa chậm với điện cực kim loại nên có tiềm năng ứng dụng lớn trong bộ nhớ sắt điện không tự xóa (FeRAM). Trong nghiên cứu này, màng mỏng sắt điện BLT được chế tạo trên đế $Pt/TiO_2/SiO_2/Si$ bằng phương pháp dung dịch. Qua đó, khảo sát sự thay đổi các đặc trưng như cấu trúc vật liệu, hình thái bề mặt, tính chất điện của màng mỏng BLT. Các đặc trưng được khảo sát bằng các hệ nhiễu xạ tia X (XRD), kính hiển vi điện tử quét (SEM), và hệ đo tính chất điện (Radiant Precision LC 10). Kết quả thu được cho thấy màng mỏng sắt điện BLT được ủ tại 725 °C có tính chất điện, cấu trúc tinh thể và hình thái bề mặt tốt nhất. Cụ thể màng mỏng BLT có độ dày 200 nm, màng mỏng sau khi ủ nhiệt không có hiện tượng nứt gãy trên bề mặt. Kết quả nhiễu xạ tia X cho thấy màng mỏng BLT đã đạt được cấu trúc hợp thức perovskite chồng lớp, có định hướng ưu tiên (117) và (006) ở nhiệt độ ⩾ 725 °C. Hơn nữa, kết quả khảo sát cấu trúc cũng cho thấy sự ảnh hưởng của pha tạp La(0,75) lên sự phát triển của hạt theo trục c của cấu trúc BLT. Kết quả phân tích ảnh SEM cho thấy kích thước hạt lớn nhất khoảng 400 nm. Phân cực dư của màng mỏng BLT ở 725 °C khoảng 10 μC/cm2 và đặc trưng điện trễ chưa bão hòa ở thế áp thấp.

*Từ khóa:* BLT, perovskite, sắt điện, bộ nhớ, màng mỏng.