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Grain growth behavior in bismuth titanate-based ceramics

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Abstract

Bismuth titanate and lanthanum-doped bismuth titanate ceramics were prepared from freeze-dried powders employing conventional solid state reaction and sintering procedures. The sintering process was carried out at 1150 °C from 4 up to 48 h. X-ray diffraction analysis showed that preferred orientation was reduced in bismuth titanate ceramic as sintering time increased while lanthanum-doped sample showed much less degree of preferred orientation and was independent of sintering time. Grain growth studies also showed that initial anisotropic grain growth rate was the main factor controlling the grain morphology, rendering the plate-shaped grain in both pure and lanthanum-doped bismuth titanate ceramics. Based on established grain growth law, pore-controlled diffusion could be the major mechanism determining the observed microstructure in these layered compounds.

Keywords: Sintering; Grain growth; Powders-solid state reaction; Bismuth titanate-based compound

1. Introduction

Pure and doped bismuth titanate ($Bi_4Ti_3O_{12}$ or BIT) have been under investigation recently due to their good electrical fatigue resistance behavior and their possible use in ferroelectric random access memories or FRAM applications.[1] A number of techniques have been employed to synthesize these materials both in thin film and ceramic forms.[2–6] For thin films, a number of research work have shown that highly *c*-axis oriented grain morphology could be produced by several processing techniques particularly the templated grain growth method which enabled measurements of anisotropic properties of these films.[7–10]

In ceramics, it has been well known that both pure and doped BIT possess plate-like grains and properties which are also orientation dependent. For example, dielectric properties along the direction perpendicular and parallel to *c*-axis were found to be quite different.[11] Hence, due to anisotropic behavior of this material, a number of researchers have fabricated BIT ceramics with grains aligned in certain direction by various techniques such as templated grain growth and tape-casting.[12] Others have found that employing external parameters such as magnetic field or pressure could also produce ceramics with oriented grains.[11–14] Inoue et al.[12] had shown that BIT ceramics with highly oriented grains could be fabricated from compacted plate-shaped powders which were originally prepared from salt solutions. However, the prepared ceramics contained large pores between well sintered plate-shaped grain colonies.[12] The authors also briefly mentioned the anisotropic grain growth behavior of sintered green compact prepared from conventionally prepared BIT powder. Based on these previous studies and the fact that grain growth kinetics and time dependence of grain morphology of BIT ceramics prepared by conventional sintering method have not been investigated in detail, this research therefore attempts to quantitatively study the effects of sintering time on microstructures, grain orientation and density of BIT ceramics. The results are discussed and compared to those of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) ceramics to elucidate the effects of lanthanum ion addition on grain growth behavior of BIT ceramics.

2. Experimental procedure

$Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ powders were prepared from binary oxides i.e. Bi_2O_3 (>98.0%, Fluka), La_2O_3 (99.99%, Cerac) and TiO_2 (>99%, Riedel-de Haën). The stoichiometric amounts of starting powders were mixed using ball milling with

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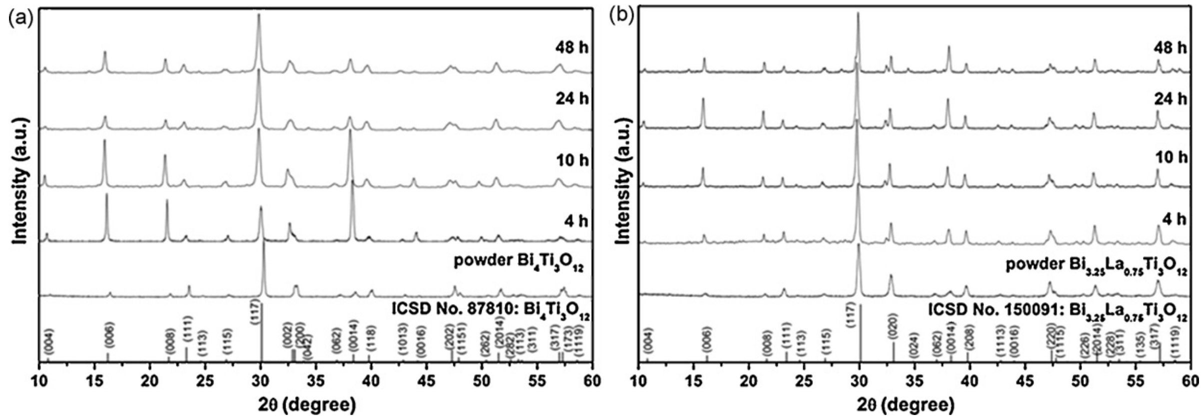

Fig. 1. X-ray diffraction patterns of calcined powder and sintered ceramics of (a) $Bi_4Ti_3O_{12}$ and (b) $Bi_{3.25}La_{0.75}Ti_3O_{12}$.

zirconia balls and distilled water for 24 h at a rate of 60 rpm. The mixtures were then transferred to a spherical flask and placed in a shell freezer. The flask was rotated in an ethanol bath for at least 1 h to produce frozen slurry, which was immediately dried in a vacuum drier for at least 24 h. After all ice was sublimated, fine freeze-dried powders were obtained. The powders were then calcined at 750 °C for 4 h before being re-ground, pressed into small pellets and sintered at 1150 °C for 4, 10, 24 and 48 h. X-ray diffraction analysis was employed to study phase formation and crystal structure of calcined powder and polished surfaces of ceramics using an X-ray diffractometer (Philips model X-pert) with CuK_α radiation. Density was measured using Archimedes method. Microstructure of ceramic surfaces thermally etched in air at 1000 °C for 15 min was investigated using a scanning electron microscope (JEOL JSM-6335F). Grain size was obtained from SEM micrographs using direct measurement of grain length and thickness across the center of each grain. Averaged values for each sample were obtained from measuring one hundred grains. For degree of grain orientation, the following equations were used

$$P_0 = \frac{\sum I_0(0\,0\,l)}{\sum I_0(h\,k\,l)} \tag{1}$$

$$P = \frac{\sum I(0\,0\,l)}{\sum I(h\,k\,l)} \tag{2}$$

In the above equations, P_0 and P are the fraction of $(0\,0\,l)$ X-ray peaks with respect to all peaks for powders and ceramics, respectively. $I_0(0\,0\,l)$ and $I(0\,0\,l)$ are the integrated X-ray $0\,0\,l$ peak intensities of powder and ceramic samples, respectively. $I_0(h\,k\,l)$ and $I(h\,k\,l)$ are their corresponding integrated intensities of all peaks within the 2θ range (i.e. 10–60°) under investigation. After P_0 and P were calculated, a Lotgering factor[15] was obtained using equation

$$F = \frac{P - P_0}{1 - P_0} \tag{3}$$

3. Results and discussion

Fig. 1(a) shows X-ray diffraction patterns of BIT ceramics. For sintering time of 4 h, the ceramic surface showed relatively high degree of preferred orientation of $0\,0\,l$-type indices. As the sintering time increased, the degree of preferred orientation decreased. Quantitatively, the $0\,0\,l$-oriented grain contribution approximated from integrated intensity of X-ray peaks relative to other grain orientation is also shown in Fig. 2. It seems therefore that for short sintering time (4 and 10 h), the compacted particles with c-axis oriented parallel to the pressing direction tended to grow and contribute to high degree of $0\,0\,l$ preferred orientation observed. At longer sintering time (24 and 48 h), the influence of grains with c-axis oriented perpendicular to pressing direction became more pronounced (Fig. 1(a)) with a corresponding reduction in $0\,0\,l$ preferred orientation (Fig. 2). These grains seemed to grow over some of the $0\,0\,l$-oriented grains, hence rendering smaller fraction of the latter on the ceramic surface. It should be noted that a slight shift of X-ray peaks of BIT ceramics compared to that of powder was probably due to instrumental error since the weight loss during sintering was found to be negligible, indicating that stoichiometry did not change and, therefore, X-ray patterns of ceramics and powder should be identical.

Fig. 1(b) shows X-ray diffraction of BLT calcined powder and sintered ceramics. Although the X-ray pattern of calcined

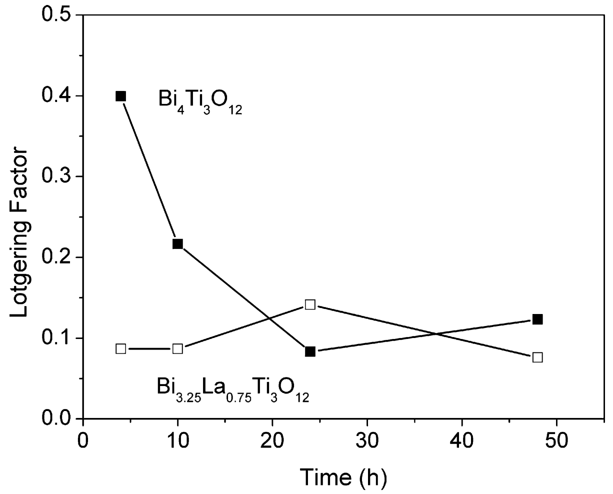

Fig. 2. Lotgering factor as a function of sintering time for BIT and BLT ceramics with respect to their calcined powders.

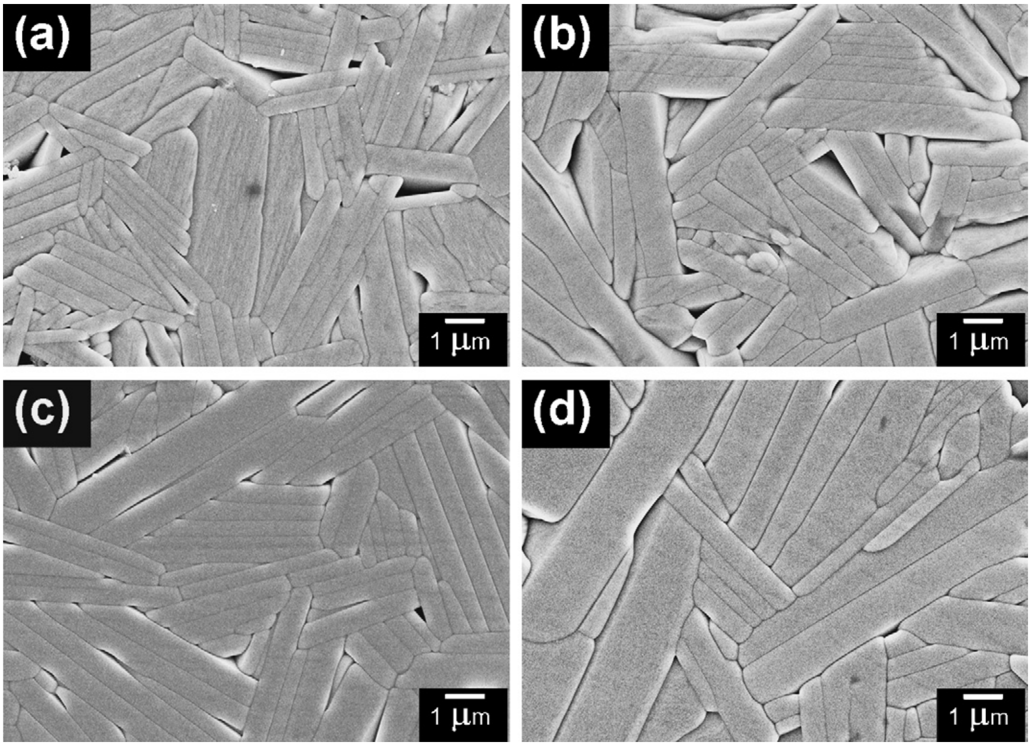

Fig. 3. SEM micrographs of thermally etched surfaces of BIT ceramics at various sintering times: (a) 4 h, (b) 10 h, (c) 24 h and (d) 48 h.

BLT powder was nearly the same as that of BIT, it could be seen that the degree of 0 0 *l* preferred orientation of BLT ceramics was much less than that of BIT ceramics when compared at the same sintering time. The effect of sintering time on degree of preferred orientation based on calculated Lotgering factor of 0 0 *l*-oriented grains is also shown in Fig. 2. It could be seen that, compared to BIT ceramics, the degree of grain orientation of BLT was nearly independent of sintering time. For long sintering period, the degree of 0 0 *l*-type preferred orientation in BIT and BLT ceramics was nearly the same. This suggested that the grain

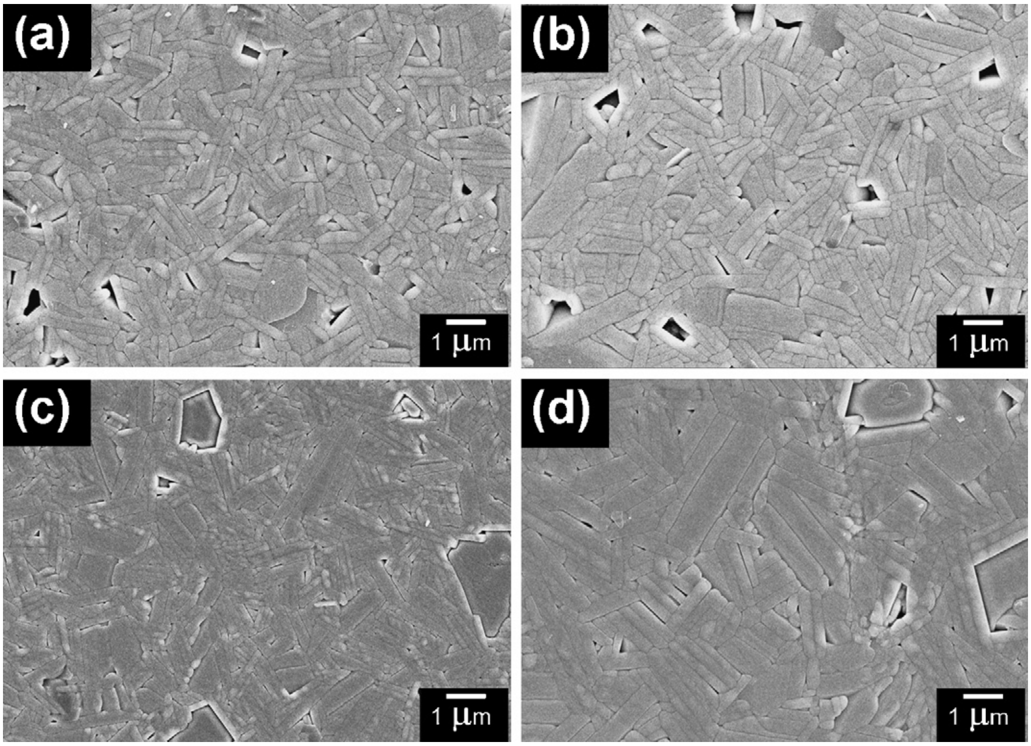

Fig. 4. SEM micrographs of thermally etched surfaces of BLT ceramics at various sintering times: (a) 4 h, (b) 10 h, (c) 24 h and (d) 48 h.

Table 1
Grain length and thickness of $Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$.

Sintering time (h)	Grain length: l (μm)		Grain thickness: t (μm)		l/t	
	BIT	BLT	BIT	BLT	BIT	BLT
4	5.88 ± 1.99	2.15 ± 0.73	0.98 ± 0.30	0.54 ± 0.13	6.00	3.98
10	8.44 ± 2.58	2.33 ± 0.66	1.46 ± 0.46	0.62 ± 0.16	5.78	3.74
24	9.62 ± 3.96	2.81 ± 1.00	1.67 ± 0.57	0.63 ± 0.15	5.76	4.45
48	10.38 ± 4.82	3.01 ± 1.21	1.77 ± 0.64	0.73 ± 0.21	5.86	4.12

Table 2
Density of $Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics.

Sintering time (h)	$Bi_4Ti_3O_{12}$		$Bi_{3.25}La_{0.75}Ti_3O_{12}$	
	Density (g/cm^3)	Relative density[a] (%)	Density (g/cm^3)	Relative density[a] (%)
4	7.55 ± 0.01	94.15	7.40 ± 0.03	96.47
10	7.41 ± 0.08	92.40	7.43 ± 0.02	96.88
24	7.31 ± 0.01	91.14	7.44 ± 0.03	96.95
48	7.38 ± 0.01	92.00	7.17 ± 0.13	93.51

[a] X-ray density of $Bi_4Ti_3O_{12} = 8.02\ g/cm^3$ and $Bi_{3.25}La_{0.75}Ti_3O_{12} = 7.67\ g/cm^3$.

growth kinetics of these two systems might be similar at long sintering time.

Figs. 3 and 4 show thermally etched surfaces of BIT and BLT ceramics, respectively. For the same sintering time, the grain size of BIT was much larger than that of BLT ceramic. As the sintering time increased, the grain size became increased both in terms of grain length and thickness. Their values are listed in Table 1. The density for both compounds did not vary much with sintering time (see Table 2). It could be observed however that the relative density of BIT ceramics was slightly less than that of BLT due to the larger plate-like grains, causing greater difficulties in having high packing density. Their low density values were also confirmed in the micrographs in which relatively high fraction of large pores was observed in BIT compared to that of BLT ceramics.

To study grain growth behavior in these compounds, the grain size in terms of grain length and thickness as a function of time was plotted and shown in Fig. 5. It could be observed that, in both BIT and BLT ceramics, the grain size along *ab*-plane initially increased abruptly and then increased more slowly at longer sintering time. Regardless of sintering time, both grain length and thickness of BIT ceramics were much larger than that of BLT ceramics. This indicates the well known effect of grain growth inhibition by lanthanum ions. To further quantify this point, the grain growth rate was obtained by fitting an empirical curve to the data points. It was found that the best fitted curve was obtained using the power function in the form $G = abt^{1-c}/(1 + bt^{1-c})$, where G is the grain size (length or thickness), t is the time, and a, b, c are the fitting constants. After the fitting, the slope was calculated to obtain instantaneous grain growth rate.

Fig. 6 shows the growth rate as a function of sintering time. It is apparent that the initial growth rate along *ab*-plane (grain length) was much faster than that along *c*-axis (grain thickness) for both BIT and BLT ceramics. This grain growth anisotropy could be largely due to the different atomic attachment/diffusion

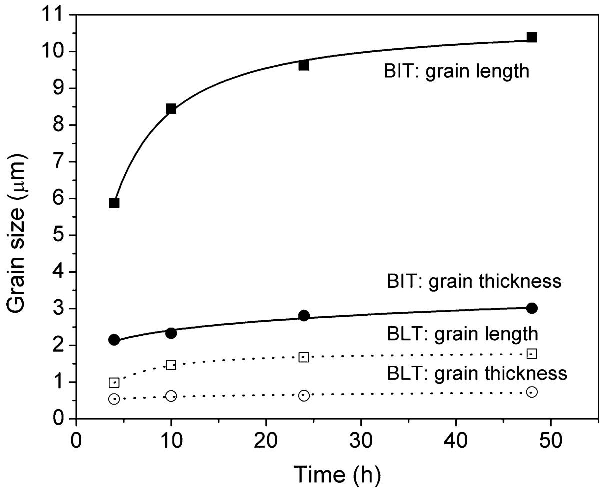

Fig. 5. Grain size of BIT and BLT ceramics as a function of sintering time.

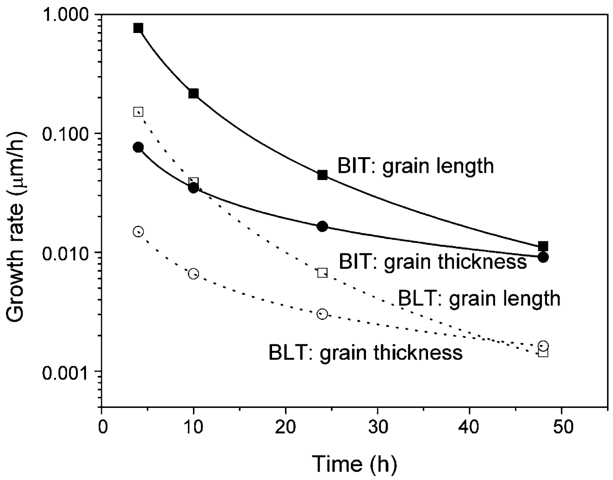

Fig. 6. Grain growth rate of BIT and BLT ceramics as a function of sintering time.

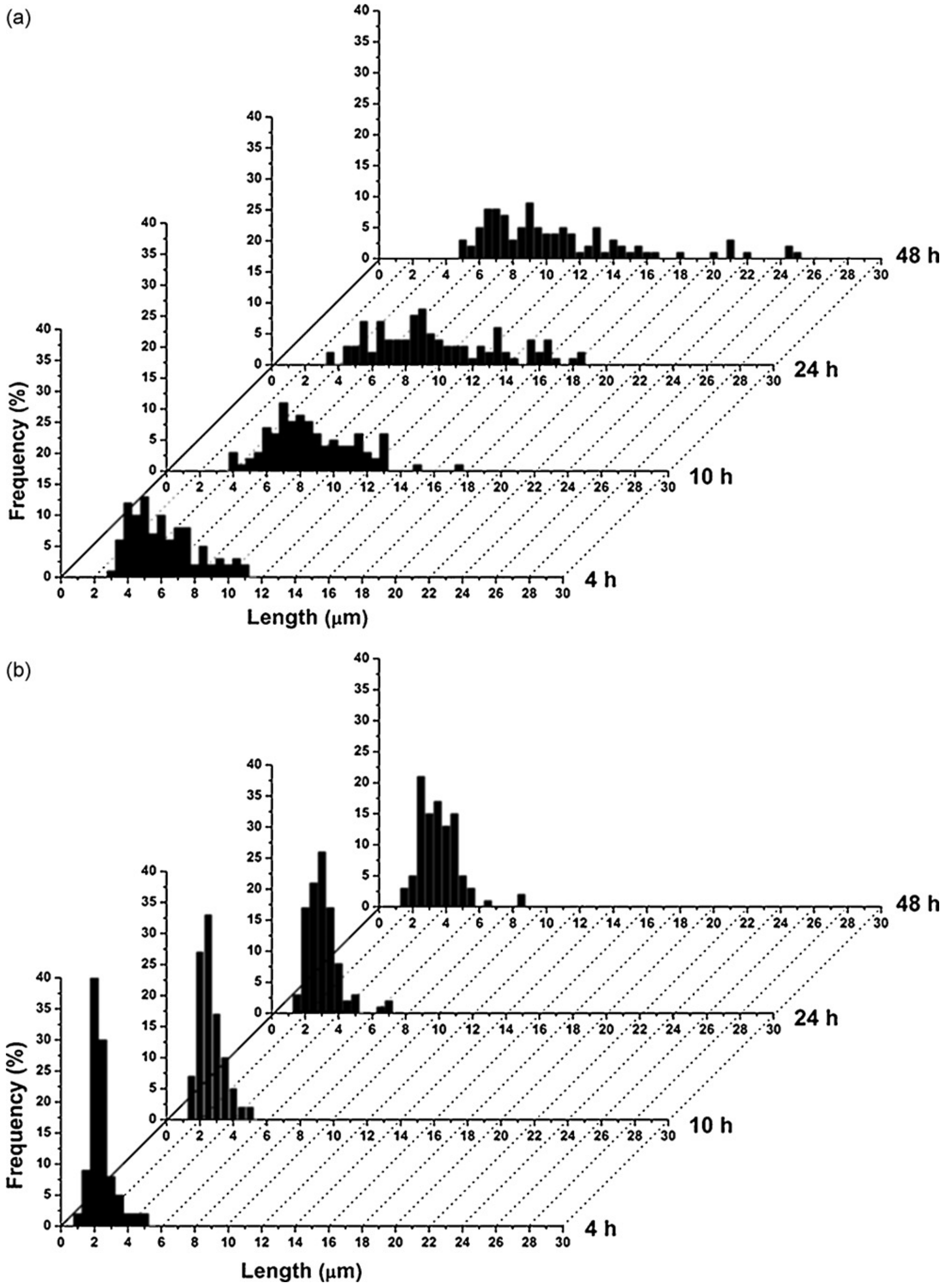

Fig. 7. Grain size distribution as a function of sintering time: (a) BIT and (b) BLT ceramics.

rates along different directions which, in turn, were influenced by the orthorhombic crystal structure of BIT and BLT. From the figure, it could be observed that the grain growth rate of BIT ceramic in both directions was about 10 times faster than that of BLT ceramic. This further proved the effectiveness of lanthanum in grain growth inhibition. As the sintering time increased, the growth rates in both directions decreased until their values became comparable at long sintering time. This reduction in grain growth rate should be expected since as the grain grew, more time would be needed to complete each atomic layer on each grain. This comparable grain growth along *ab*-plane and *c*-axis at long sintering time in both BIT and BLT ceramics also seemed to play a large part in determining the amount of preferred orientation in these ceramics. Hence, the initial anisotropic grain growth rate seemed to be the main factor causing the plate-shaped microstructures in both BIT and BLT ceramics. For long sintering time, the grain growth rate became more isotropic with reduced preferred orientation as observed in this study. The effect of lanthanum on grain growth inhibition also resulted in narrower grain size distribution in BLT ceramics compared to that of BIT ceramics, as shown in Fig. 7.

In terms of grain growth mechanism in BIT and BLT ceramics, attempts to find the values of exponent m in the grain growth law i.e. having a relationship $G^m - G_0^m = kt$,[16] where G_0 is grain size at time $t = 0$ and k is a constant, were not very successful. Fig. 8 shows the plot of a straight line fit through data

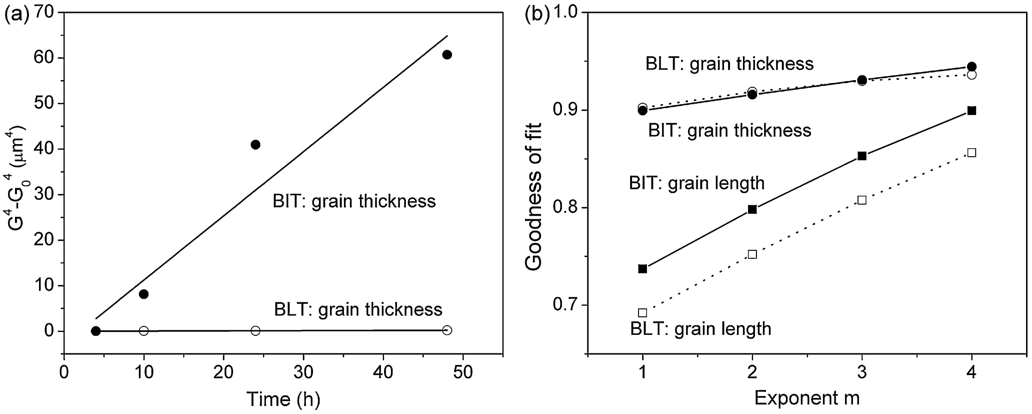

Fig. 8. Grain growth law applied to BIT and BLT ceramics: (a) linear fitting for $m = 4$ and (b) goodness of fit as a function of exponent m.

points (using $m = 4$ in this case) and the goodness of fit (having an ideal value of 1) as a function of exponent m. It could be seen that the best fit, though still having relatively large residual error, was found for m equals 4 which corresponded to the pore-controlled surface diffusion or boundary-controlled diffusion due to coalescence of second phase.[16] However, the samples investigated in this study were mostly single phase so it was unlikely that the latter mechanism would play much role. Hence, pore-controlled surface diffusion may be a major mechanism in this material. Care should be taken however that other diffusion mechanisms may also play a role in these materials. The difficulties in applying grain growth law to BIT and BLT ceramics were due to the fact that these materials possessed anisotropic grain growth behavior as well as the fact that the grain growth law was established based on the assumption that the material must be a homogeneous compact with isotropic grain boundary energy and isolated spherical pores at the grain boundary. These properties were not closely followed in BIT and BLT ceramics due to their un-equiaxed grains. Nevertheless, based on the information obtained in this study, the rate controlling factors of grain growth could be the interfacial energy as well as the mobility of lanthanum ions. Further detailed investigation of lanthanum ion diffusion in BIT ceramic would be beneficial.

4. Conclusions

The $Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics sintered at various sintering times up to 48 h were successfully fabricated. X-ray diffraction analysis showed that while $Bi_4Ti_3O_{12}$ ceramics showed greater 0 0 *l*-type preferred orientation than $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics at short sintering time, both materials had similar degree of 0 0 *l*-type preferred orientation at longer sintering period. In both $Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics, the anisotropic grain growth rate was observed at short sintering period while at long sintering time, the growth rate along *ab*- and *c*-plane became comparable. This study showed that the plate-shaped morphology in $Bi_4Ti_3O_{12}$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics was mainly the results of initial anisotropic grain growth rate. Sintering these ceramics at longer time could render a material with more isotropic microstructure with reduced preferred orientation.

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