Lanthanum-doped $Bi_4Ti_3O_{12}$ ceramics prepared by high-pressure technique*

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We present an effective way in this paper to increase the density of lanthanum doped bismuth titanate ceramics, $Bi_{4-x}La_xTi_3O_{12}$ (BLT), thereby significantly improving the performance of the BLT ceramics. Dense BLT ceramicses, $Bi_{4-x}La_xTi_3O_{12}$ (x = 0.25, 0.5, 0.75, 1.0), are prepared by using nanocrystalline powders fabricated by a –gel method and high-pressure technique. The microstructures of the BLT ceramicses prepared separately by conventional-pressure and high-pressure techniques are investigated by using x-ray diffraction and transmission electron microscope. The influence of La-doping on the densification of bismuth titanate ceramics is investigated. The experimental results indicate that the phase compositions of all samples with various lanthanum dopings sintered at 900 °C possess layer-structure of $Bi_4Ti_3O_{12}$. The green compacts are pressed under 2.5 GPa, 3.0 GPa, 3.5 GPa and 4.0 GPa, separately. It is found that the density of BLT ceramics is significantly increased due to the decreasing of porosity in the green compacts by high-pressure process.

Keywords: bismuth titanate ceramics, lanthanum doping, high-pressure technique, densification

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1. Introduction

In recent years, with the increase in popularity of nonvolatile random access memories (NvRAMs), more and more attention has been paid to the study of ferroelectric materials.[1−7] Bismuth layer-structured ferroelectrics are thought to be promising materials for NvRAMs applications due to their excellent fatigue-free nature and other electric properties.[8] Among them, bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT) is known to be a typical kind of layer-structured ferroelectric material and has been widely investigated because of its good properties, such as fast switching speed, high fatigue resistance of the device with metal electrodes and good retention, owing to the large spontaneous polarization, and almost fatigue-free property.[9−13] In addition, its high Curie temperature (675 °C) makes it a suitable candidate for high temperature applications. Recent studies have revealed that doping BIT by lanthanide series can improve the ferroelectric properties of the materials.[14,15]

Lanthanum-doped bismuth titanate ($Bi_{4-x}La_xTi_3O_{12}$ (BLT)) ceramics has been conventionally prepared by a solid-state reaction process, where a mixture containing Bi_2O_3 and TiO_2 as well as La_2O_3 was ball milled, calcinated at an intermediate temperature and finally sintered at a high temperature.[16] This conventional method requires a high calcination temperature, usually leading to inevitable crystal particle coarsening and aggregation of the BLT ceramics. The presence of hard particle agglomerates will also result in poor microstructure and properties of the BLT ceramics. Many efforts have been made to avoid this problem, such as lowering the calcination temperature, increasing bisque density and shortening sintering time.[17−19] However, these methods failed to solve this problem fundamentally.

In the present paper, a sol–gel process is used to synthesize the BLT powders and high-pressure technique is adopted to prepare the dense BLT green compacts in order to lower sintering temperature and eliminate the macro-holes of the BLT ceramics. The ob-

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jective of this work is to promote the densification of BLT ceramics and improve mechanical and physical properties of the prepared materials.

2. Experimental procedure

A sol–gel process was used to prepare $Bi_{4-x}La_xTi_3O_{12}$ (x = 0.25, 0.5, 0.75, 1.0) powders. The temperature of colloidal sol was kept at about 60–80 °C for 120 h. Then the xerogel was gained. The xerogel was then calcinated at 900 °C and thus the BLT crystal powders were obtained. The scheme of the preparation of the BLT powders fabricated by sol–gel method is shown in Fig. 1.

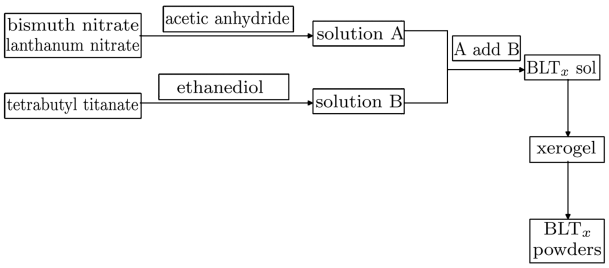


Fig. 1. Schematic of preparation process of BLT powders by sol–gel method.

A high-pressure technique was employed to prepare the green compacts under 2.5 GPa, 3.0 GPa, 3.5 GPa and 4.0 GPa at room temperature, separately. The high-pressure preparations were conducted in a cubic anvil high-pressure apparatus with a sample chamber of 18 mm on an edge under high pressure. Then, the green compacts were sintered at 900 °C for 0.5 h. Additionally, the BLT green compacts serving as a reference specimen were prepared under conventional pressure (150 MPa) and then were sintered at 900 °C for 0.5 h, which were also synthesized for investigating the densification behaviour of BLT ceramics prepared at high pressure.

The densities of all sintered BLT ceramicses were measured by using the Archimedes method and then compared with their theoretical densities. The crystal structures of the sintered samples were characterized by x-ray diffraction (XRD) (D/max 2500) with Cu K_α radiation. Transmission electron microscope (TEM, H-800)) was used to evaluate the average sizes of the BLT powders. A scanning electron microscope (SEM, JSM-5310) was used to observe the surface morphologies and hole structures of the resulting BLT ceramicses.

3. Results and discussion

The XRD patterns of $Bi_{4-x}La_xTi_3O_{12}$ (x = 0, 0.25, 0.5, 0.75, 1.0) powders synthesized by sol–gel method and calcinated at 900 °C are shown in Fig. 2. It is indicated that after calcinated at 900 °C, the phase compositions of all the powders with various lanthanum dopings are composed of single phases with a bismuth layer-structured ($Bi_4Ti_3O_{12}$). Figures 3(a)–3(d) show the TEM images of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT0.75) powders calcinated at 900 °C for different times. It can be found that the morphology of the BLT crystal is spherical and the resulting particle sizes are relatively uniform except for a small number of particles with big sizes existing in some regions, which may be caused by uneven heating. The average particle sizes of the powders calcinated at 900 °C for different times can be measured directly from Figs. 3(a)–3(d) to be about 3, 8, 22, and 55 nm, respectively. As can be seen in Fig. 3, the grain sizes of the BLT powders increase gradually with the increase of calcination time.

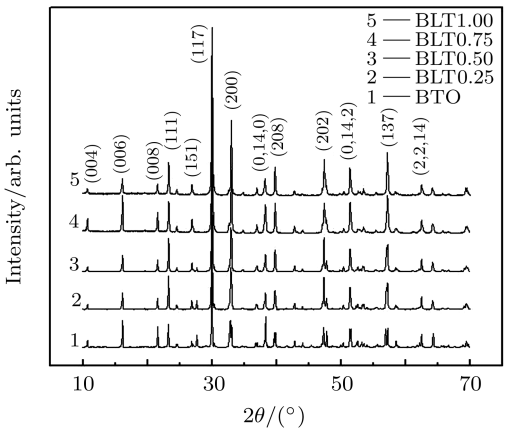


Fig. 2. The XRD patterns of $Bi_{4-x}La_xTi_3O_{12}$ (x = 0, 0.25, 0.5, 0.75, 1.0) samples calcinated at 900 °C for 0.5 h.

Figures 4(a) and 4(b) show the scanning electron microscopy (SEM) images of the sintered samples prepared under conventional pressure. It can be seen that there exist many macro-holes in the samples with sizes about 10–20 μm. The macro-holes with larger sizes may be associated with the existence of gas holes, which formed when the green compacts were prepared under conventional pressure. The existence of these macro-holes will result in poor mechanical and physical properties of the BLT ceramics. It can be observed that some white defects also exist in these samples and their quantities and sizes are similar to those macro-holes (Fig. 4(a)). The higher magnification SEM im-

age of a white defect (Fig. 4(b)) reveals that there exist some micro-holes inside of the white defects. The average sizes of these micro-holes are smaller than 1 μm. At the same time, plate-like BLT grains with an average size of about 1 μm are also found inside of the white defects. It has been reported that the existence of plate-like grains would reduce the density of BLT ceramics.[19] Thus, we can deduce reasonably that the macro-holes may result from the existence of these plate-like grains.

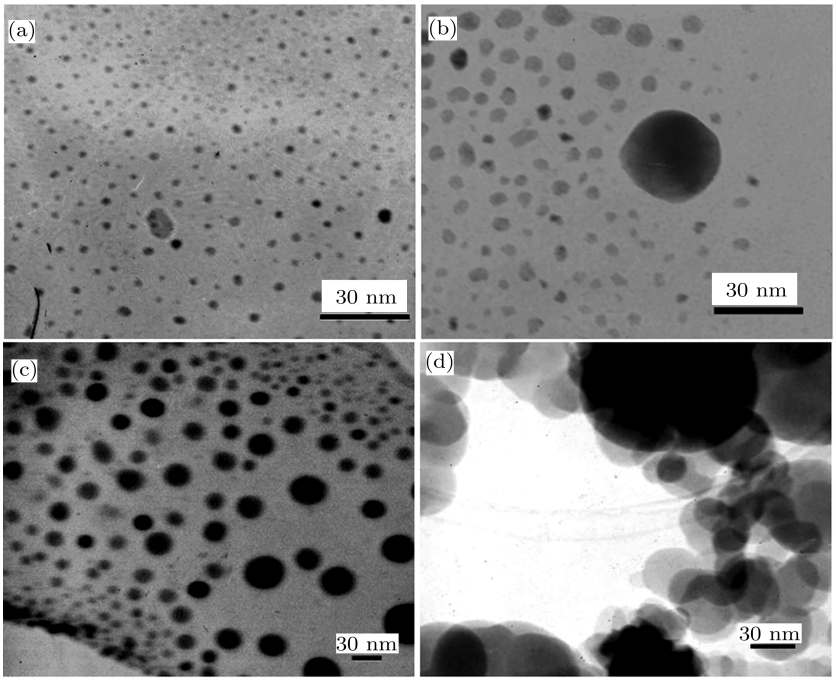


Fig. 3. TEM images of BLT0.75 powders calcinated at 900 °C for different times: (a) 10 min, (b) 20 min, (c) 30 min, and (d) 60 min.

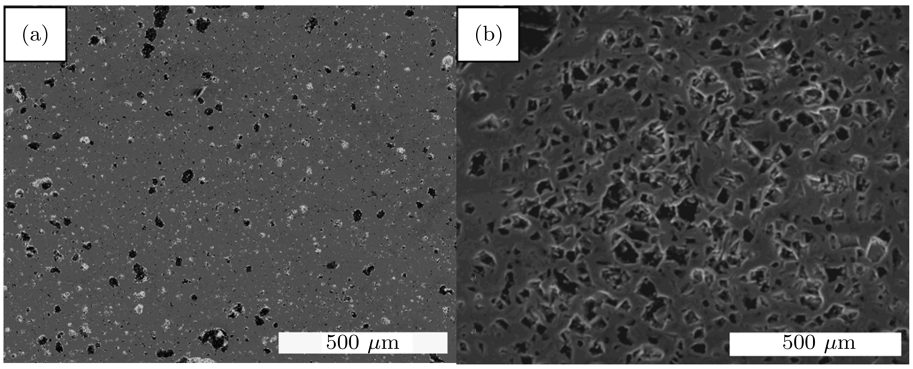


Fig. 4. The SEM images of BLT0.75 ceramics ($P = 150$ MPa, $T = 900$ °C, $t = 0.5$ h) magnified (a) 100 times and (b) 1000 times.

The SEM images of the sintered samples prepared at high pressures are shown in Fig. 5. One can see that there are almost no macro-holes in the samples. Additionally, the densities of sintered BLT ceramics at 2.5 GPa, 3.0 GPa, 3.5 GPa and 4.0 GPa are found to be 74%, 79%, 82% and 85% of their corresponding theoretical densities, respectively. Whereas, the measured density of sintered BLT ceramics prepared under conventional pressure is found to be only about 62% of its corresponding theoretical density. This result indicates that high pressure can significantly increase the densification of BLT ceramics, moreover, the density of BLT ceramics is gradually promoted with the increase of the pressure, and the pressure of 4.0 GPa yields the highest density of the sintered ceramics. The increase of the density of ceramics should be attributed to

the decreasing of porosity in specimens due to high-pressure process. Therefore, the improved mechanical and physical properties of materials result from the enhancement of the densification of BLT ceramics, which is just expected.

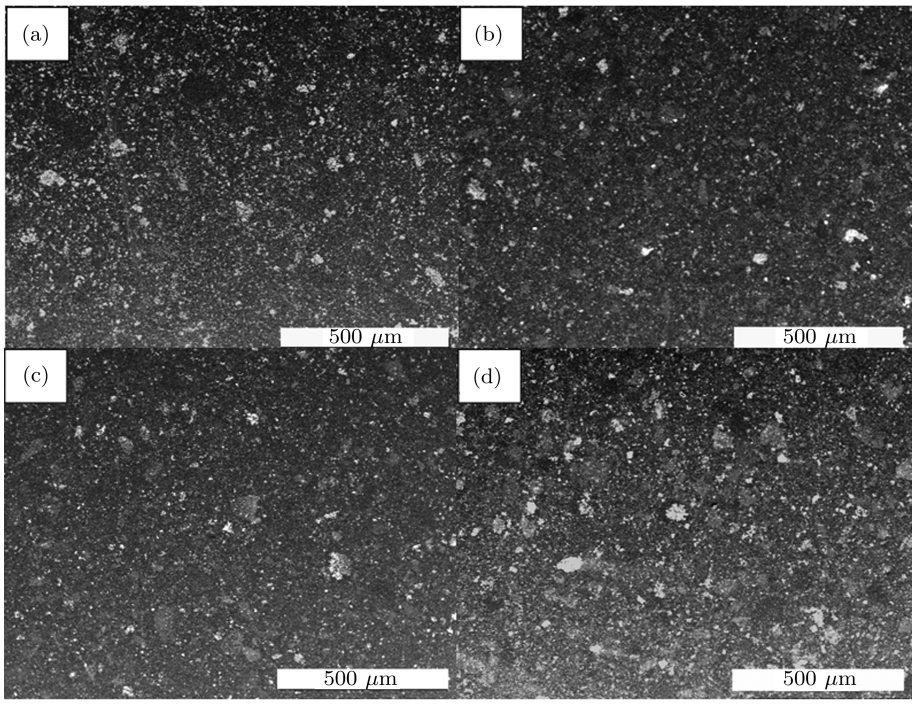


Fig. 5. The SEM images of BLT0.75 ceramicses prepared under different conditions: (a) 2.5 GPa, 900 °C /0.5 h; (b) 3.0 GPa, 900 °C /0.5 h; (c) 3.5 GPa, 900 °C /0.5 h; (d) 4.0 GPa, 900 °C /0.5 h.

Based on the study of Kingery,[20] the concave bubbles will be constricted as the convex bubbles grow, i.e., the bubbles and the edges of the grains are always moving towards the curvature centre of the boundary curve. The constriction of the bubble (the densification process of the material) will occur when the ratio of bubble size to grain size is smaller than a critical value. More bubbles with larger sizes are formed when the green compacts are prepared under conventional pressure. The increase of the sizes of the BLT powders cannot satisfy the condition of the densification which leads to the formation of "secondary bubbles" with convex edge. The diffusion of these "secondary bubbles" will result in the growth of bubbles and finally cause the production of the macro-holes. Under the action of high-pressure, the sizes of bubbles and grains in the sintering process can satisfy the condition of the densification, i.e. the concave bubbles are constricted. This may be the real reason why the macro-holes can be eliminated at high pressure.

There are more white defects, whose sizes are larger. Among the white defects the largest one can reach 50 μm. The sizes of grains inside of the white defects are about 2 μm as shown in Fig. 6, which are larger than those outside. The white defects with micro-holes are related to the pressure of the preparation of the green compacts. The quantities and the sizes of the white defects in the samples prepared under high-pressure are larger than those prepared under conventional pressure. So these white defects are related to the heterogeneity of stress distribution in the process of the preparation of the green compacts.

There exist several stress concentration areas in the green compacts prepared under high pressure when the isostatic pressure technique is not adopted. These stress concentration areas will influence the rate of the growth of the grains in the sintering process due to the existence of high stress, which will provide a driving force for the growth of the grains. Thus, it will result in the growth of grains and the occurrence of micro-defects.[21]

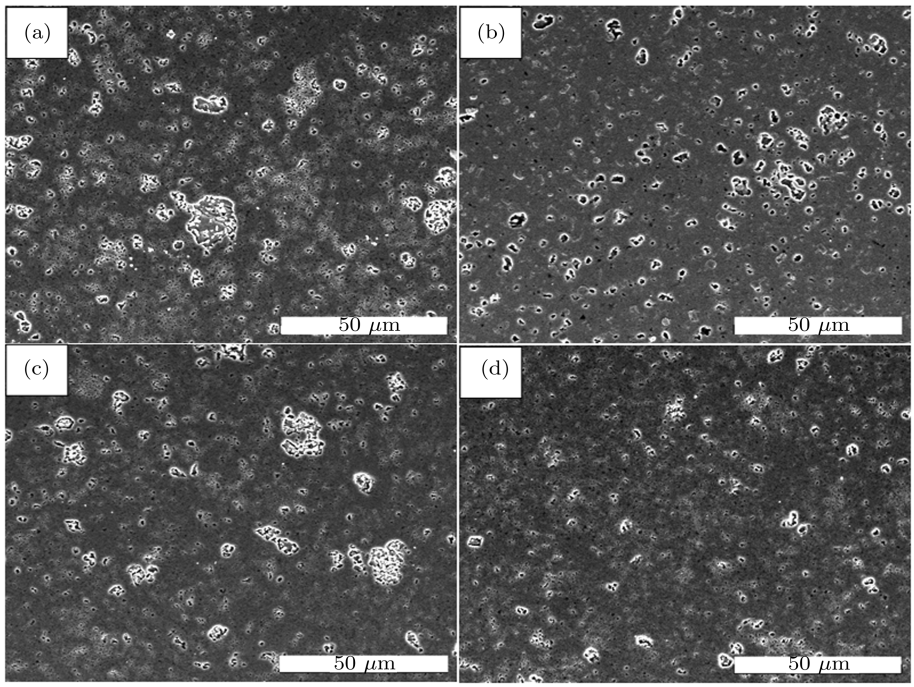


Fig. 6. The SEM images of BLT0.75 ceramics prepared under different conditions: (a) 2.5 GPa, 900 °C /0.5 h; (b) 3.0 GPa, 900 °C /0.5 h; (c) 3.5 GPa, 900 °C /0.5 h; (d) 4 GPa, 900 °C /0.5 h.

Besides, it can also be observed that inside of the white defects there are a large number of the BLT grains growing faster than those outside (Fig. 7). The energy dispersive spectroscopy (EDS) analysis shows that the lanthanum-rich area has a relatively high content of lanthanum. (Fig. 8). It can be seen in Tables 1 and 2 that lanthanum-rich area has a greater weight percentage of lanthanum and atomic percentage, which are about 7.96% and 2.83%, respectively. These micro-holes may result from the enrichment of the rare-earth metal. That may be associated with the increase of the active property of the BLT grain surface due to the enrichment of the rare-earth metal. Thus, it enhances the rate of the growth of the grains and increases the number of micro-holes.

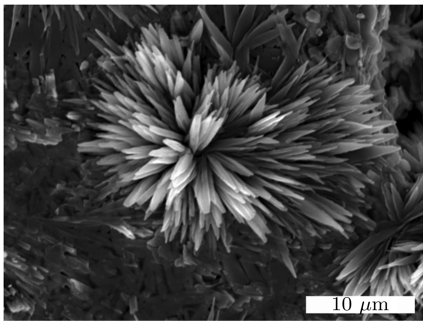


Fig. 7. The SEM image of La-rich area.

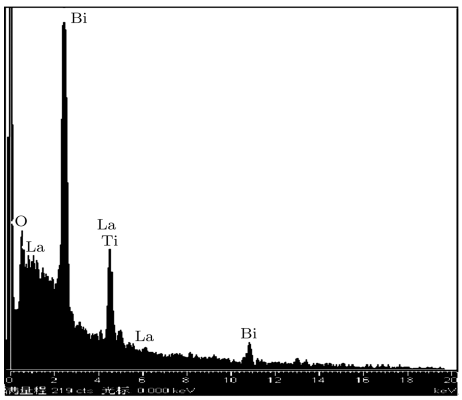


Fig. 8. The EDS analysis of La-rich area.

Table 1. The EDS of La-rich area.

element	weight percentage (%)	atomic percentage (%)
O	23.18	71.45
Ti	11.94	12.29
La	7.96	2.83
Bi	56.92	13.43

Table 2. The EDS of BLT ceramics.

element	weight percentage (%)	atomic percentage (%)
O	19.53	67.75
Ti	12.09	14.01
La	4.83	1.36
Bi	63.54	16.88

4. Conclusion

The high-pressure technique has proved to be useful for improving the densification of BLT ceramics. SEM images show that there are many macro-holes in the samples of the BLT ceramics prepared by conventional pressure technique, which will result in poor mechanical and physical properties. In order to eliminate the macro-holes, the high-pressure technique is employed, which was applied to the case of lower sintering temperature and shorter sintering time. There are almost no macro-holes in those samples prepared under high pressure. However the micro-holes resulting from the aggregation and the partly growth of the BLT grains cannot be eliminated. Besides, inside of the white defects there are a large number of the BLT grains growing faster than those outside. That may be associated with the increase of the active property of the BLT grain surface due to the enrichment of the rare-earth element.

Moreover, in the high-pressure process, the nucleation rate is increased due to the reduced energy barrier for nucleation, and the reduced growth rate due to the decrease of diffusivity. Because of the decreasing of porosity in specimens by high-pressure process, the density of ceramics is significantly increased, and therefore, the dense ceramics can be obtained.

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