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Effect of increasing lanthanum substitution and the sintering procedures on the properties of $SrBi_4Ti_4O_{15}$ ceramics

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Abstract. **Lanthanum-substituted $SrBi_4Ti_4O_{15}$ (SBTi) ceramic, that is $SrBi_{4-x}La_xTi_4O_{15}$ (SBLTi), samples were calcined by solid-state reaction and densified using the microwave sintering and conventional sintering techniques. Their structural, morphological and mechanical properties were investigated. The microwave sintered samples showed high densities like 95% of the theoretical density with short duration exposures. Compared with SBTi ceramics and other lanthanide-substituted compositions, the incorporation of La^{3+} results in clear improvement in properties for SBLT ($x \sim 0.75$) with respect to the values of hardness and Young's modulus of the microwave sintered samples (8.8–12.5 and 160–180 GPa) are higher than that for conventional sintered (8–10 and 135–155 GPa) samples.**

Keywords. **Microwave sintering; La-substituted SBTi ceramics; mechanical properties.**

1. Introduction

In recent years, bismuth layer-structured ferroelectrics (BLSF) have attracted much attention for their potential use in high-temperature piezoelectric devices and ferroelectric random access memories because of their relatively high Curie point (T_c), lead-free composition and excellent fatigue endurance property.[1] ABO_3-type ferroelectric $Pb(Zr, Ti)O_3$ (PZT) has been extensively investigated for the characteristics of large remanant polarization, moderately low coercive field and high Curie temperature, but it has the drawbacks of poor fatigue endurance and large coercive field. Bismuth-layered pervoskite compounds such as $SrBi_4Ti_4O_{15}$ (SBTi) or $SrBi_2Nb_2O_9$ (SBN) are free from lead and can be the alternative to PZT owing to their excellent ferroelectric properties, particularly with respect to their fatigue resistance to polarization switching. BLSFs have a crystal structure containing interleaved bismuth oxide $(Bi_2O_2)^{2+}$ layers and pseudo-perovskite blocks which contains BO_6 octahedra and is generally formulated as $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$. In this notation A represents a mono-, bi- or trivalent ion, B denotes a tetra-, penta- or hexavalent ion and m is the number of BO_6 octahedra in each pseudo-pervoskite block (m = 1–5).[2]

Substitution with rare-earth elements is necessary to improve the SBTi ferroelectric properties. $SrBi_{4-x}La_xTi_4O_{15}$ (SBLTi) ceramic samples are prepared by the solid-state reaction. However, the high temperatures used during the sintering can cause problems in the stoichiometry of the final product owing to the volatility of Bi, and hence an alternative process is often needed. Some methods used to obtain bismuth-layered pervoskite ceramic precursors are the hydrothermal, sol–gel and co-precipitation synthesis. However even after preparing precursors with these chemical methods, the sintering in general is done with the conventional heating. An attractive alternative for these problems is the microwave sintering technique, which often eliminates the stoichiometry problems by accomplishing the process at much lower sintering temperatures over a short period of time.

In the microwave process, the heat is generated internally within the material on account of the absorption of microwave energy instead of originating from external sources, and hence there is an inverse heating profile. The heating is very rapid as the material is heated by energy conservation rather than by energy transfer, which occurs in conventional techniques. Microwave sintering has many advantages over conventional methods.[3] Some of these advantages apart from energy saving include reduction in the process time and lower process temperature that leads to a fine microstructure resulting in improved mechanical properties. From application point of view, lower processing temperature is an important parameter to get better properties. For Bi-containing materials, microwave sintering is more important as it could reduce Bi volatilization, thereby preserving required stoichiometry even after sintering. Here the properties of SBLTi ceramics processed by microwave sintering as well as by conventional sintering is reported and a comparative study is made.

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2. Experimental

Synthesis of the material was carried out with a powder mixture containing equimolar amount of 99.9 + % pure Bi_2O_3, $SrCO_3$, La_2O_3 and TiO_2 (Aldrich). The powder mixture was ball milled in deionized water and then calcinated at 750°C for 4 h. Calcined powder was uniaxially pressed into circular pellets. These pellets were sintered at 1190°C for 2 h in ambient atmosphere in a conventional furnace to achieve conventionally sintered samples.

The microwave sintering was conducted using a 1.3 kW, 2.45 GHz multimode microwave furnace. Density and microstructural information were obtained on microwave sintered and conventional sintered samples by the Archimedes principle and scanning electron microscopy (SEM), respectively. The formation and phase purity of the compound were performed by the X-ray diffraction (XRD) technique. XRD patterns were recorded using an Inel-Equinox powder diffractometer with Co-Kα radiation in a wide 2θ range of 20–70° at a scanning rate of 1 deg min^{-1}.

Indentation experiments were performed using a Triboscope® Nanomechanical Testing System (Hysitron Inc., Minneapolis, MN, USA). The system was fitted with a three-sided pyramid shape Berkovich tip with diameter 100 nm. Thus, the hardness, H, could be determined from the maximum indentation load, P_{max}, divided by the contact area,[4] i.e.,

$$H = \frac{P_{max}}{A}, \tag{1}$$

where the contact area (A) is a function of the penetration depth, h. The reduced modulus E_r^* is given as

$$E_r^* = \frac{\sqrt{\pi}}{2}\frac{\beta S}{\sqrt{A}}, \tag{2}$$

where S is the stiffness of the test material, which can be obtained from the initial unloading slope by evaluating the maximum load and the maximum depth, i.e., $S = dP/dh$. β is a shape constant that depends on the geometry of the indenter and is 1.034 for the Berkovich tip. The reduced modulus E_r is related to the modulus of elasticity E_s of the test specimen through the following relationship

$$\frac{1}{E_r^*} = \frac{1-\nu_i}{E_i} + \frac{1-\nu_s}{E_s}.$$

Here, the subscript i indicates a property of the indenter material and ν is Poisson's ratio.

For a diamond indenter tip, E_i is 1140 GPa and ν_i is 0.07. The tests were conducted under load control, using peak loads in the range between 0 and 2000 μN.

3. Results and discussion

3.1 *Structural*

XRD patterns of microwave and conventional sintered $SrBi_{4-x}La_xTi_4O_{15}$ (where x = 0.25, 0.5, 0.75 and 1) ceramics are shown in figure 1. It indicates that lanthanum substitution does not change the structure of SBTi or generate new phases. No significant difference in the lattice parameters was observed in materials with various contents of La. The position of the diffraction peaks are in good agreement with the standard orthorhombic pattern. The similarity of XRD patterns are indicative of the similarity of chemical valance involved and close values of the ionic radii between La^{3+} and Bi^{3+} ions. The crystalline size of the conventional and microwave sintered samples were calculated by the Debye–Scherrer formula. The crystalline

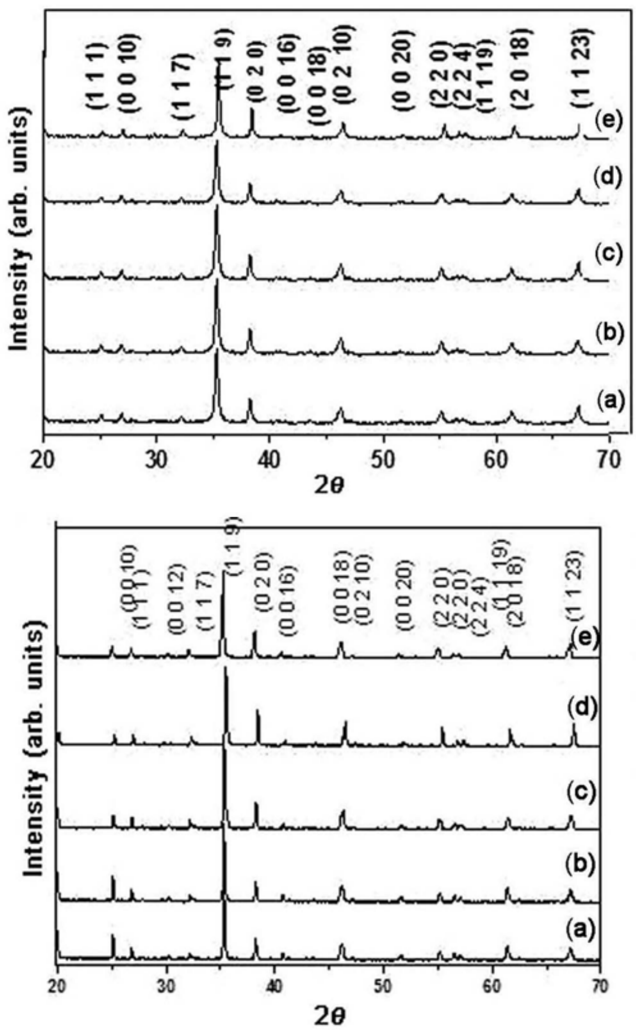

Figure 1. X-ray diffraction pattern of microwave (top) and conventional sintered (bottom): (**a**) $SrBi_4Ti_4O_{15}$, (**b**) $SrBi_{3.75}La_{0.25}Ti_4O_{15}$, (**c**) $SrBi_{3.5}La_{0.5}Ti_4O_{15}$, (**d**) $SrBi_{3.25}La_{0.75}Ti_4O_{15}$ and (**e**) $SrBi_3La_1Ti_4O_{15}$.

size of the conventional sintered samples ranged from 610 to 790 Å, which is more than microwave sintered samples that is 420–480 Å. It is found that the crystallite size of the microwave sintered samples is less than conventional sintered samples. It is evident from the XRD pattern as each peak broadening is more in microwave sintered samples than conventional sintered samples. Chemical composition of the La-substituted SBTi samples was same before heat treatment for both conventional and microwave process. There might be slight variation in conventional sintered samples due to longer time and high-temperature heat treatment. Bi and oxygen volatization will be more during the heat treatment in conventional process than microwave process.

3.2 *Microstructural*

The microstructure of the SBLTi samples sintered by microwave and conventional routes are as shown in figures 2 and 3. SEM images of SBLTi samples show grains in the form of platelets. This orientation is typical of Aurivillius phases and is due to the polycrystalline nature of the samples. SEM micrographs show that conventionally sintered samples got grains that are non-uniform and of platelet-like shape. The microstructure of conventional sintered SBTi ceramics shows the presence of different grain size ranges as well as microcracks as reported by Patro,[5] whereas microwave sintered samples are highly densified and got uniform grain size. Uniaxially pressed circular samples of SBLTi pellets of 0.4 g mass and 8 mm diameter were conventionally sintered in air at 1190°C for about 2 h to achieve above 90% of relative density. Similar samples were sintered in a microwave furnace at different temperatures and different time durations. It was found that there is obvious densification in the microwave field even at 1150°C for 30 min heating. The relative density of conventional and microwave sintered samples is shown in table 1. Maximum relative

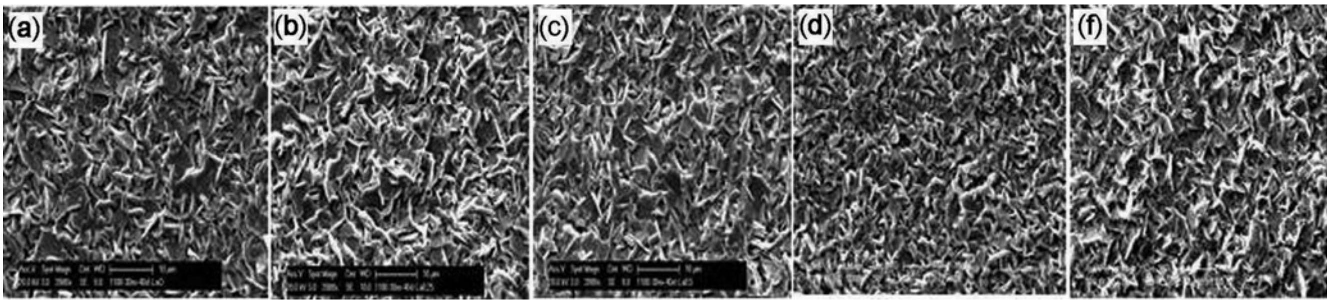

Figure 2. SEM micrographs of microwave sintered: (**a**) $SrBi_4Ti_4O_{15}$, (**b**) $SrBi_{3.75}La_{0.25}Ti_4O_{15}$, (**c**) $SrBi_{3.5}La_{0.5}Ti_4O_{15}$, (**d**) $SrBi_{3.25}La_{0.75}Ti_4O_{15}$ and (**e**) $SrBi_3La_1Ti_4O_{15}$.

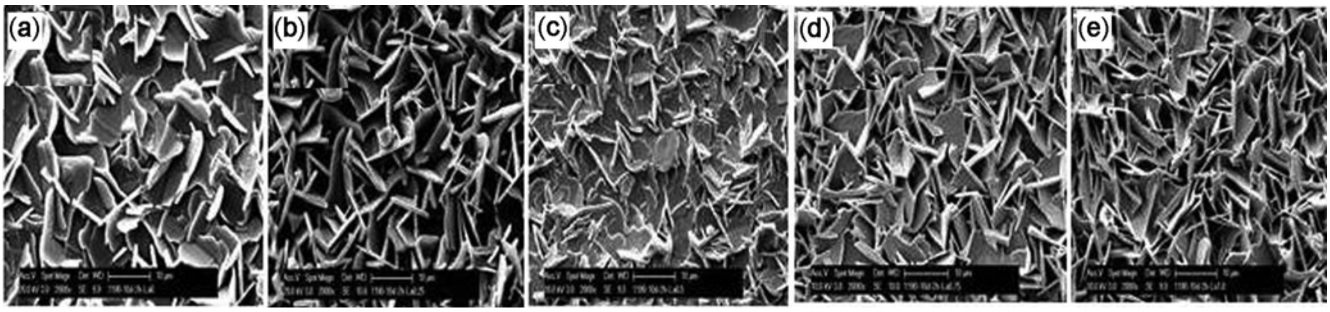

Figure 3. SEM micrographs of conventional sintered: (**a**) $SrBi_4Ti_4O_{15}$, (**b**) $SrBi_{3.75}La_{0.25}Ti_4O_{15}$, (**c**) $SrBi_{3.5}La_{0.5}Ti_4O_{15}$, (**d**) $SrBi_{3.25}La_{0.75}Ti_4O_{15}$, and (**e**) $SrBi_3La_1Ti_4O_{15}$.

Table 1. Relative density of microwave and conventional sintered SBTi and La-substituted SBTi ceramics.

Samples	Relative density (%)					Sintered temperature (°C)
	La 0	La 0.25	La 0.5	La 0.75	La 1	
Microwave sintered	92.7	92.5	94.5	96.5	88.4	1150
Conventional sintered	90.6	91.6	92.8	93.1	88.1	1190

density of 96.5% is obtained at 1150°C for 30 min of microwave sintering. By contrast, conventional sintering of SBTi is slow. For example, 4 h sintering at 1150°C led to 80.5% of relative density. To get high densification conventionally, samples are to be sintered at high temperatures and for longer period. The average grain size of the conventional and microwave sintered samples was found to range from 8 to 10 and 4 to 6 μm, respectively. The increase in grain size for conventional samples is not fully understood and needs further investigation but could be due to a phase with greater wettability resulting in a liquid phase that is clearly visible in the micrograph of figure 3. The grain size observed in microwave processed samples is smaller and denser than the conventional one. The longer soak time required in conventional sintering as well as its slow heating rate also could accelerate grain growth at the cost of nucleation. The density of the SBLT with $x = 0.5$ and 0.75 is higher than that of original SBTi ceramics in both conventional and microwave sintered processed samples. Percentage of doping and microwave sintering plays a vital role to enhance the density. In clear, as the doping percentage increases (up to 0.75) density of the ceramic samples increased in both conventional and microwave sintered samples compared to undoped ceramic samples. Microwave sintered samples got high density than conventional sintered samples due to advantage of microwave energy. The heating is very rapid as the material is heated by energy conservation rather than by energy transfer which occurs in conventional techniques. Microwave sintering has many advantages over conventional methods. Some of these advantages apart from energy saving include reduction in process time and lower process temperature that leads to a fine microstructure resulting in improved properties. On the contrary, SBLT with $x = 1$ is having lower density for both conventional and microwave sintered samples. Decreasing density for La = 1 is due to structural distortion and smaller grain size. From this it is clear that the excess substitution of La suppresses the grain growth during the sintering by pinning of grain boundaries, thus resulting in poorer density. This significant decrease in grain size with the increase in the La content is supported by previous studies.[6,7] The shift in XRD pattern for La = 1 is clearly evident for structural distortion. The rapidity of microwave sintering method could be a reason for suppression of grain growth resulting in a finer and uniform microstructure. The same phenomenon was also observed by Fang *et al*.[8] The substantially enhanced densification in the microwave sintered samples can be considered as the cause for their fairly enhanced mechanical properties.

3.3 *Mechanical properties*

Figure 4 shows the typical measured load–displacement curve of SBLTi ceramics. Figures 5 and 6 show the

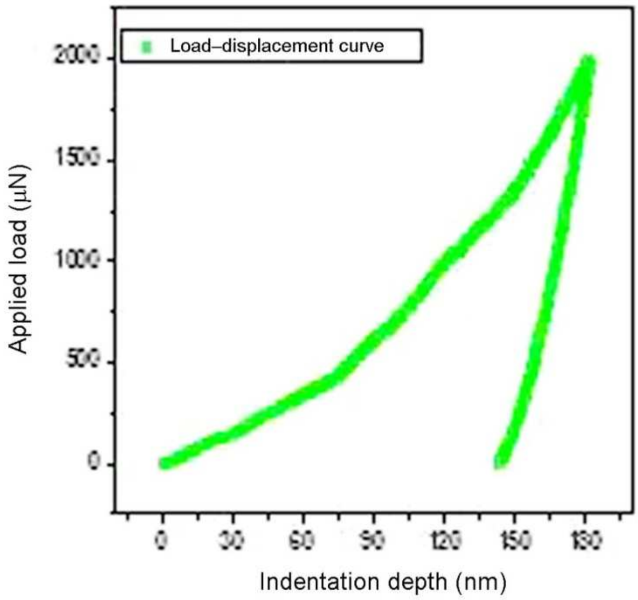

Figure 4. Typical load-displacement curve for La-substituted SBTi ceramics.

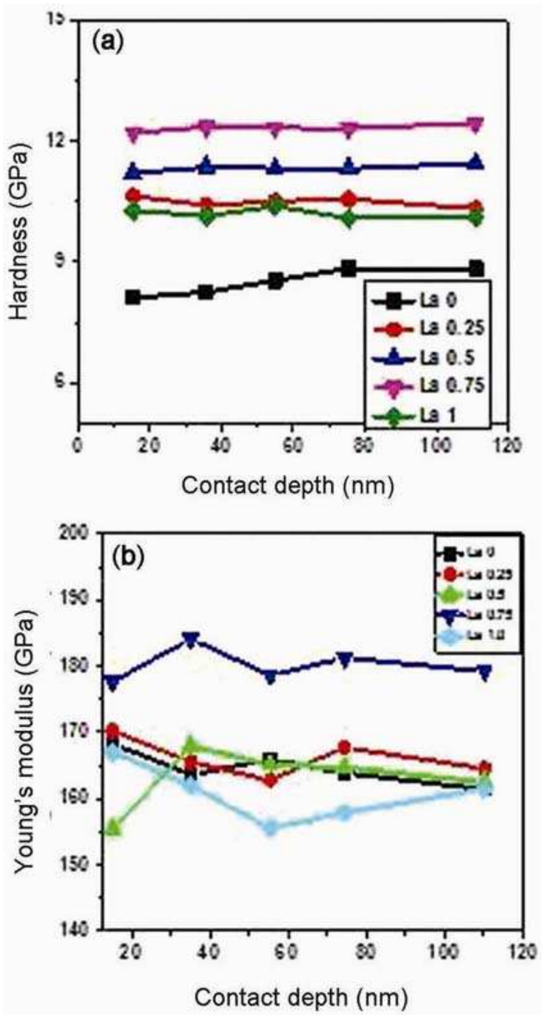

Figure 5. (**a**) Hardness and (**b**) Young's modulus of microwave sintered SBLTi ceramics as a function of contact depth.

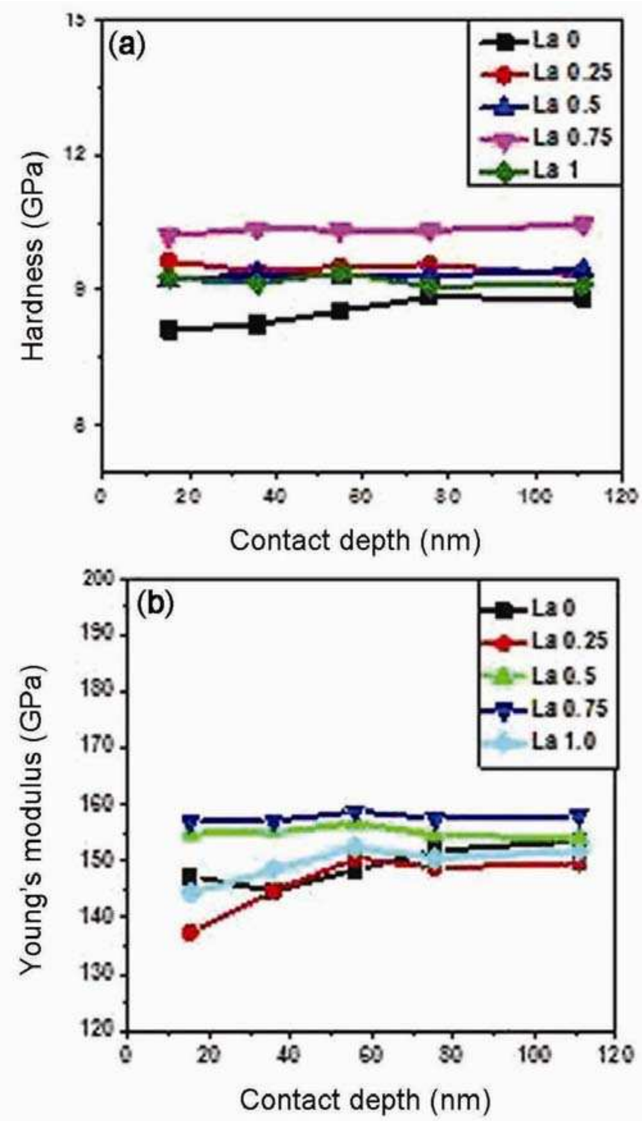

Figure 6. (**a**) Hardness and (**b**) Young's modulus conventional sintered SBLTi ceramics as a function of contact depth.

mechanical properties of the conventional and microwave sintered samples of SBLTi ceramics measured by the nanoindentation technique. The hardness and Young's modulus values are the average of the five indentations at different places to avoid microstructural effect on mechanical properties. It should be mentioned that mechanical properties of SBTi ceramics are previously not reported. The hardness of the microwave sintered samples ranged from 8.8 to 12.5 GPa, whereas for the conventional sintered samples is 7–10 GPa. It could be noted from figures 5 and 6 that as the La content increases the hardness also increases in both processes. La (or x) ~ 0.75 shows good mechanical properties with both microwave and conventional sintered samples. On the other hand, La ~ 1 is shows inferior mechanical properties compared to $x = 0$–0.75 and this could be due to higher porosity. As it is known that the mechanical properties of the materials depend on the microstructure and porosity. These results highlight that the hardness of the SBLTi ceramics increases with deceasing porosity. Young's modules of the microwave and conventional sintered samples are ranged from 160 to 180 and 135 to 155 GPa, respectively. High Young's modulus values reflect the lower defect density and finer grains of the samples. Moreover, it is interesting to observe that Young's modulus values are depending on the grain size of the samples. The samples that are having less grain size are having higher Young's modulus. Same phenomena was observed by Ricote and Pardo.[9] From these results it follows that the hardness is independent of grain size and Young's modulus seems to decrease with increase of grain size. The improved mechanical strength achieved in microwave processing could be attributed to small grain size and uniform microstructure where crack centers like large pores and defects are few. Density measurements are supporting the mechanical properties of the microwave sintered samples.

For both the conventional and microwave sintered cases, it is quite remarkable that, the highest hardness and Young's modulus values are obtained with samples having $x = 0.75$. It is true that density, microstructure and composition influence mechanical properties. Yet, this coincidence as observed previously[10] reinforces the suspicion that mechanical properties are related at least in these systems, to give best results for both the properties in the same composition when composition is varied systematically.

4. Conclusions

$SrBi_{4-x}La_xTi_4O_{15}$ (where $x = 0.25$, 0.5, 0.75 and 1) ceramics were prepared by solid-state reaction and sintered through conventional and microwave sintering techniques. The microwave sintering of La-substituted SBTi ceramics leads to higher densification and fine microstructure in much shorter time duration than conventional sintering. Compared with SBTi ceramics and other Lanthanide-substituted compositions, the incorporation of La^{3+} results in clear improvement in properties for SBLT (x ~ 0.75) leads to the development of a material with a hardness and Young's modulus. That means the microwave sintering influences only the extrinsic factors like density, grain size, grain morphology and crystallite size. The results of La-doped SBTi microwave sintered samples are desirable for device fabrication of SBTi-based ceramic capacitors and actuators.

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