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Microstructure and microwave dielectric properties of $BaLa_4Ti_4O_{15}$ ceramics with template particles

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Abstract

$BaLa_4Ti_4O_{15}$ (BLT) ceramic has excellent microwave dielectric properties with high dielectric constant (ε_r) and high quality factor ($Q \times f$). However, BLT has the negative temperature dependence of resonant frequency (τ_f). In this study, single phase and plate-like BLT particles were prepared via a molten salt synthesis using NaCl, KCl and NaCl–KCl flux. Plate-like BLT template particles mixed with powders synthesized by solid-state reaction were uniaxially pressed and sintered. Sintered ceramics with template particles showed anisotropy in the microstructure and the crystalline phase. In the microwave dielectric properties, τ_f and ε_r increased with an increasing amount of template particles, and $Q \times f$ were nearly equal to that of specimens without template particles.

Keywords: Molten salt synthesis; Grain growth; Sintering; Dielectric properties; $BaTiO_3$ and titanates

1. Introduction

Grain orientation technique has been used to improve the poling efficiency of piezoelectric materials, particularly in systems where the number of possible symmetry directions is small. As alternative techniques such as hot pressing, hot forging and templated grain growth (TGG) offers the possibility of fabricating grain-oriented polycrystalline ceramics that exhibit single crystal-like properties. It has been shown that oriented template particles can be used to develop textured microstructures using TGG in some electroceramics.[1] There are only a few reports about microwave dielectric ceramics concerned with TGG method. For the TGG method, particles with anisotropy like columnar or plate-like in shape are required as template. We have confirmed that sintering of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ with the columnar particles lead to anisotropic grain growth, and their microwave dielectric properties exhibited large anisotropy.[2,3] However, highly texture development of columnar particles needs a uni-directional alignment. Therefore, plate-like particles are more easily formed than columnar particles. Plate-like particles are the most suitable to obtain orientation.

It is known that $BaLa_4Ti_4O_{15}$ (BLT) ceramics have excellent microwave dielectric properties with high dielectric constant $\varepsilon_r = 45$ and high quality factor $Q \times f = 41{,}000$ GHz. However, the temperature coefficient of resonant frequency (τ_f) is -26 ppm/°C.[4] For the resonator applications, material with a near zero τ_f is needed. Generally, improvement of τ_f has been achieved by changing composition such as formation of solid solution or adding another material with opposite sign of τ_f for the compensation. In most cases, it can cause severe degradation to ε, and/or and $Q \times f$ even though τ_f is improved significantly. Consequently, another method is required to improve τ_f without decrease of ε_r and $Q \times f$.

BLT has a large anisotropy in the crystal structure. BLT belongs to layer perovskite-type structure and has a trigonal crystal system with lattice parameters are $a = 5.572$ Å and $c = 22.48$ Å. Hence, BLT crystals tend to show plate-like appearance. Therefore, it can be a candidate material for application of TGG method. In the present paper we report the preparation of BLT plate-like crystals and the fabrication of grain-oriented BLT ceramics.

2. Experimental procedure

BLT particles were prepared via a molten salt synthesis using NaCl, KCl and equimolar NaCl–KCl flux. $BaCO_3$ (99.87%), TiO_2 (99.8%) and La_2O_3 (99.9%) dehydrated at 1000 °C were weighed according to $Ba_4La_4Ti_4O_{15}$ formula and mixed with equal weight of the NaCl or KCl salts by ball milling for 24 h in ethanol using zirconia balls. The mixture after drying was

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heated to temperatures in the range from 1100 to 1300 °C for 0–6 h and cooled in air.

The products were washed with hot deionized water and sonicated for 20 min several times in order to remove the salts and deagglomerate the clustered particles. The BLT particles obtained by molten salt synthesis were mixed with BLT powders synthesized by solid-state reaction at 1000 °C for 2 h and added binder (polyvinyl alcohol). The powder after uniaxially pressing at a pressure of 98 MPa was sintered at 1600 °C for 2 h. The phases of sintered specimens were identified by powder X-ray diffraction (XRD) using Cu Kα radiation (X'pert-MPD; Philips). The surfaces of specimens were observed by scanning electron microscopy (SEM; JSM-5200, JEOL). The apparent density was measured by Archimedes' method. The dielectric constant (ε_r), unloaded Q value and temperature coefficients of the resonant frequency (τ_f) between 20 and 80 °C were measured using a pair of parallel conducting Ag plates under the TE_{011} mode using Hakki and Coleman's method[5] (8720ES, Agilent Technologies).

3. Results and discussion

3.1. Preparation of BLT particles

Fig. 1 shows TG-DTA thermographs for BLT–NaCl mixtures. The endothermic peak at 370 and 520 °C is associated with dehydrated $La(OH)_3$ as shown in Table 1 (Eq. (1)). The starting material La_2O_3, transformed to $La(OH)_3$ before heating.[6] The intense endothermic peak at 795 °C corresponds to the melting point of NaCl. Fig. 2 shows the XRD pattern of the powders prepared at various reaction temperatures. At 600 °C, the XRD shows the presence starting materials. La_2O_3 were rehydroxylated to $La(OH)_3$ before heating. With the increasing of temperature, $La_2Ti_2O_7$ and La_2TiO_5 phases increased.

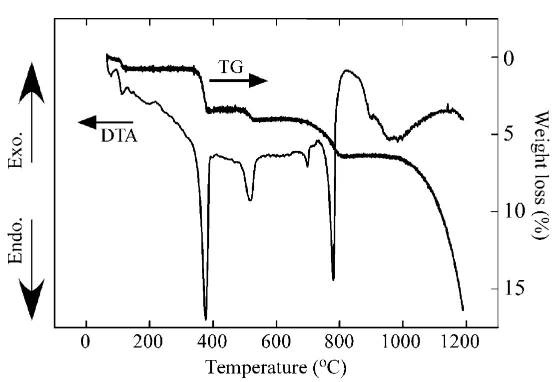

Fig. 1. DTA-TG curves of BLT–NaCl.

Table 1
Formation process of BLT

$La(OH)_3 \rightarrow La_2O_3 + H_2O$	(1)
$La_2O_3 + 2TiO_2 \rightarrow La_2Ti_2O_7$	(2)
$La_2O_3 + TiO_2 \rightarrow La_2TiO_5$	(3)
$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$	(4)
$BaTiO_3 + La_2Ti_2O_7 + La_2TiO_5 \rightarrow BaLa_4Ti_4O_{15}$	(5)

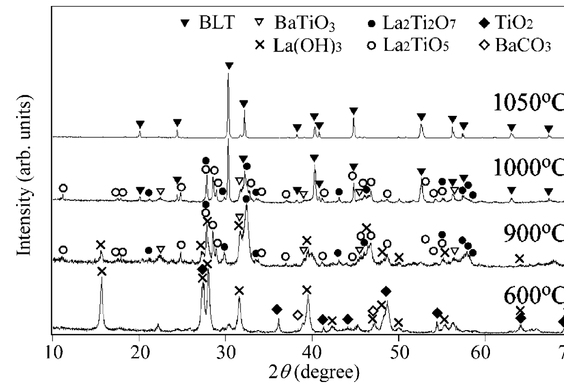

Fig. 2. XRD patterns of powders subjected to heat treatment at various temperatures for 2 h using NaCl.

At 1000 °C, formation of BLT phase has started, and above 1050 °C, single phase BLT has been identified. Therefore, it is found that the formation of $BaLa_4Ti_4O_{15}$ phase is completed at 1050 °C in the NaCl flux. Accordingly, the exothermic peak at 850 °C observed in Fig. 1 is the formation peak of $La_2Ti_2O_7$ and La_2TiO_5. The exothermic peak at 1000 °C is the BLT formation peak. From the results of Table 1 and Fig. 1 revealed the reaction sequence of BLT synthesized in NaCl molten salt.

3.2. Molten salt synthesis

Fig. 3 shows SEM micrographs of the powder prepared by NaCl, KCl and NaCl–KCl fluxes. Hexagonal plate-like particles were obtained in all conditions. By using NaCl or NaCl–KCl flux, single phase BLT was obtained. In the powder prepared with KCl flux, some large rectangle plate-like crystals identified as $La_2Ti_2O_7$ were found. It was because the crystal grew before the reaction of Eq. (4) (shown in Table 1) completely took place. The particle prepared with NaCl flux was the largest size of the three, the second was KCl–NaCl, and the smallest size was KCl flux. These results suggest that particle size was not correlated to melting or eutectic temperature. Generally, it is known that the higher preparation temperature results in the larger particle size. In the present study, the particle prepared at higher temperature

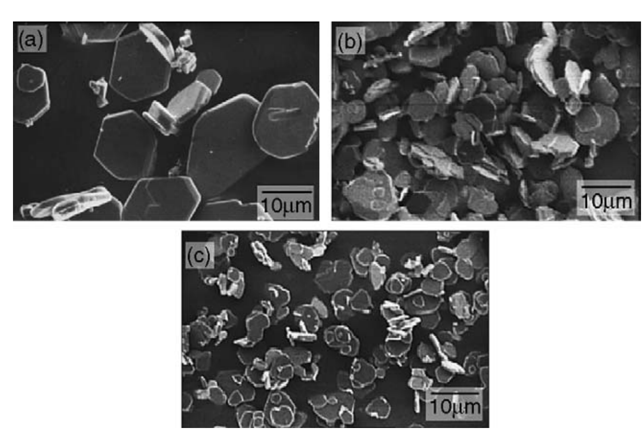

Fig. 3. SEM micrographs of powders obtained after heat treatment at 1300 °C using (a) NaCl; (b) NaCl–KCl; (c) KCl.

was larger in size. The particle size of BLT prepared with NaCl at 1100 and 1300 °C were 10.20 and 14.21 μm, respectively. In contrast, with NaCl–KCl flux grew little like 9.65 to 10.20 μm. The particle using KCl flux heated at 1100 and 1200 °C were about 7 μm, at 1300 °C was 11.20 μm. This abrupt change was caused by the growth of $La_2Ti_2O_7$ crystals. The aspect ratio of the template particles must be high, its size must be large and homogeneous. The reaction product heat treatment at 1100 and 1200 °C with NaCl show many BLT fine particles. It is observed that the volume of small particles decreased with the increase of heating temperature as shown in Fig. 3. The powder heated at 1300 °C consists of plate-like grains only. On heating at high temperatures, the fine particles merge to form larger particles. The particle size of grains prepared at 1250 and 1300 °C were of the same size. Hence, the preparation temperature of template particles using NaCl flux was optimized to 1250 °C in all subsequent studies.

3.3. Sintering of BLT with plate-like crystals

Relative densities of all samples were above 94%. XRD measurements (Fig. 4) and SEM (Fig. 5) observations revealed that the plate-like BLT grains aligned perpendicular to the pressing direction. The 0 0 1 0 peaks dominate the diffraction pattern for the natural surface of the samples with the increasing the template concentrations. For the surface of the polished pellets, dominant peak is the same with and without template particles whereas 0 0 1 0 peaks became stronger and 1 1 0 peaks became weaker. During sintering, oriented BLT grains acted as seeds for the anisotropic grain growth within the specimens. Because of large degree of freedom for grain growth the surface grew larger, as compared to the template inside the specimen.

Secondary phase of $La_2Ti_2O_7$ was found in the specimen with the template concentrations of 50 wt%. The $La_2Ti_2O_7$ is also oriented in the specimen because only the 0 0 4 peak is identified in Fig. 4. The crystal structure of $La_2Ti_2O_7$ also has anisotropy as follows; layer perovskite-type structure, monoclinic crystal system with lattice parameters $a = 7.803$, $b = 25.687$, $c = 5.542$ (Å).[7] Hence, $La_2Ti_2O_7$ tends to form rectangular grains.

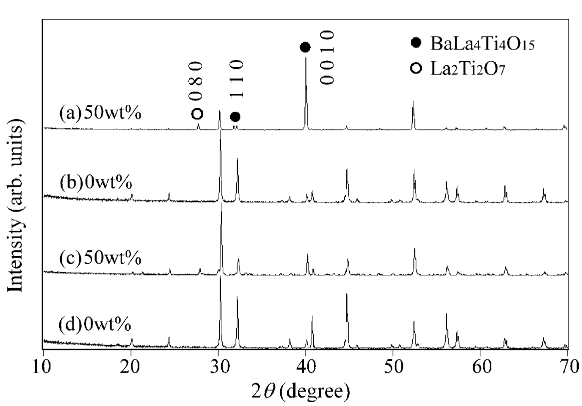

Fig. 4. XRD patterns of the (a, b) natural surface (c, d) polished surface of BLT prepared with plate-like crystal sintered at 1600 °C for 2 h.

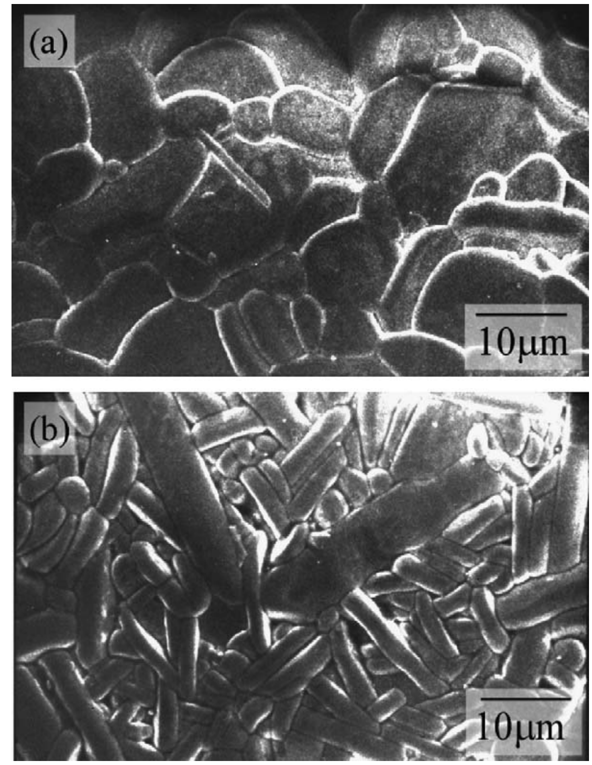

Fig. 5. SEM micrographs of the surface of the specimen sintered at 1600 °C for 2 h (a) without and (b) with plate-like crystals. The pressing direction in normal to the plane of SEM picture.

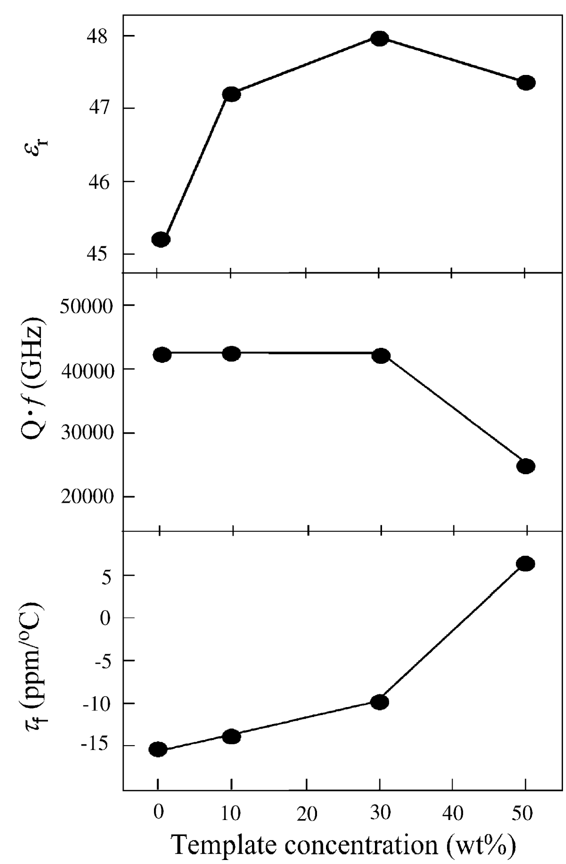

Fig. 6. Microwave dielectric properties of $BaLa_4Ti_4O_{15}$ as a function of plate-like crystals in the starting mixture.

3.4. Microwave dielectric properties

Fig. 6 shows microwave dielectric properties of BLT sintered with plate-like particles. τ_f increased with an increasing amount of template particles. The ε_r of samples sintered with template exhibited higher than those of specimens without template particles. The $Q \times f$ value was equivalent to those of specimens without template particles. Specimen with 50 wt% template showed different properties from the specimens with lower concentration of templates. The τ_f increased abruptly and the $Q \times f$ decreased. The reason is as follows. τ_f of non-oriented $La_2Ti_2O_7$ shows negative value as −10 ppm/°C[8] whereas ⟨0 1 0⟩ oriented $La_2Ti_2O_7$ demonstrate high positive temperature coefficient of capacitance of 188 ppm/°C in the direction parallel to the oriented *b*-axis.[7] $La_2Ti_2O_7$ was oriented ⟨0 1 0⟩ direction in the specimen as shown in Fig. 4. Remarkable increase of τ_f attributed to the formation and orientation of $La_2Ti_2O_7$. Decrease of $Q \times f$ also caused by presence of $La_2Ti_2O_7$.

4. Conclusions

Single phase, hexagonal plate-like $BaLa_4Ti_4O_{15}$ particles were prepared by molten salt method using NaCl and NaCl–KCl flux. The preparation with NaCl flux at 1250 °C resulted in the particle size of approximately 15 μm. The ceramic specimen prepared by uniaxial pressing with the BLT plate-like particles showed anisotropy in the crystalline phases and the microstructure. With an increasing amount of template particles up to 50 wt% ε_r increased whereas $Q \times f$ value were nearly equal to that of specimens without template particles. τ_f of specimen including template particles increased with an amount of template particles. These results indicated that the anisotropy of BLT could be used as one of the means for controlling the dielectric properties.

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