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Analysis on the temperature dependent structural properties of Li_2CO_3 doped (Ba,Sr)TiO_3 ceramics

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Abstract We have fabricated various amount of Li_2CO_3 doped (Ba,Sr)TiO_3 (BST) ceramics for LTCCs (Low Temperature Co-fired Ceramics) applications through the conventional sintering method. By introducing Li_2CO_3 into BST ceramics, the sintering temperature was decreased from 1350°C to 900°C. In this study, we discussed the crystalline and structural properties of Li_2CO_3 doped BST ceramics. By scanning X-ray diffraction analysis, we found that 1, 3, and 5 wt% Li_2CO_3 doped (Ba,Sr)TiO_3 ceramics have perovskite structure without any pyrochlore phases. Frequency dependent dielectric properties were analyzed and discussed. Scanning Electron Microscopy (SEM) images depending on the sintering temperature and dopants were prepared and discussed. The crystalline and dielectric properties of Li_2CO_3 doped (Ba,Sr)TiO_3 were discussed.

Keywords Ferroelectrics · Dielectric response · SEM · BST

1 Introduction

Ferroelectrics are very attractive materials for wide range of applications. For the high frequency applications, they are very promising materials due to their nonlinear behavior of dielectric permittivity in electric field. Especially, (Ba,Sr)TiO_3 (hereafter BST) materials for low temperature co-fired ceramics (LTCCs) technologies have been attracted attention to the field of microelectronic component applications due to its high dielectric permittivity, tunability, low dielectric losses and small leakage current density [1, 2]. LTCCs technologies have a unique ability to integrate passive components such as resistors, capacitors and inductors into a monolithic package for System on Packaging (SOP) applications.

However, the pure BST and BST-base materials are commonly sintered at high temperature over the 1350°C, which is too high to be used for the silver electrodes. To co-fire the ceramic and electrodes, electrode materials have to bear up against this high thermal energy. To endure the high thermal energy, expensive and noble electrode materials such as palladium and platinum were required. However, platinum electrodes have relatively lower electrical conductance and much expensive than silver electrodes. If the sintering temperature of BST ceramic can be lowered under 900°C, silver electrode was able to be employed as the inner electrodes of LTCCs.

Many researches have been conducted to reduce sintering temperature of functional ceramics by adding dopants such as B_2O_3 [3], La_2O_3 [4], $LiCO_3$ [5], CuV_2O_6 [6], and CuO [7]. By adding dopants to the ferroelectric or dielectric materials, dielectric permittivity can be decreased, while loss tangent increased. Moreover, by adding glass frits to the functional ceramics, the sintering temperature can be lowered drastically, while their dielectric properties were degraded by a large margin [8]. According to our previous study, the sintering temperature was decreased from 1350°C to 900°C by doping the Li_2CO_3 to the BST ceramics [9].

In this study, we investigated the microstructure and electrical properties of various amount Li_2CO_3 doped BST ceramics sintered at 900°C.

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2 Experiments

To make the BST powders, $BaCO_3$, $SrCO_3$ and TiO_2 powders with high purity of 99.9% were used as raw materials. The raw materials were weighed and calculated to fabricate $(Ba_{0.5}Sr_{0.5})TiO_3$ composition. The powders were mixed by employing the wet-milling process for 24 h and dried at 120°C for 24 h. The impurities and organic components were burned out at 600°C for 1.5 h and then calcined at 1100°C for 2 h and then slowly cooled down to room temperature with the rate of 3°C/min. The calcined Li_2CO_3 doped BST powders were granulated with 100 mesh sieve to uniform the powder size. The Li_2CO_3 doped BST ceramic pellets were fabricated by employing the 12 Φ mold with pressure of 1 ton. The fabricated Li_2CO_3 doped BST ceramic pellets were sintered at various temperature from 900°C to 1350°C for 2 h.

The crystalline structure of the Li_2CO_3 doped BST ceramic were analyzed by X-ray diffraction pattern. X-ray diffraction 2θ scans were measured by employing the *Rigaku X-ray diffractometer* with Cu-Kα source. To investigate the frequency dependent dielectric permittivity and dielectric loss, *HP 4284A precision LCR meter* was employed. The dielectric permittivity and dielectric loss were measured from 1 kHz to 100 kHz. The electrical properties of Li_2CO_3 doped BST ceramics were measured at room temperature by employing *Keithely 6517A electrometer/high resistance meter*. The electrical resistivity of various amount of Li_2CO_3 doped BST ceramics was calculated in the linear section of electric field dependent leakage current density characteristics by considering its geometry. The microstructure of Li_2CO_3 doped BST ceramics was investigated by employing the Field Emission Scanning Electron Microscopy (FE-SEM).

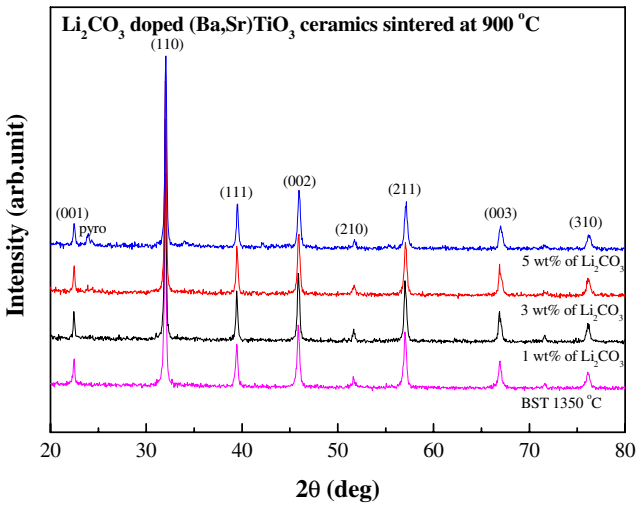

Fig. 1 X-ray diffraction pattern of pure BST ceramic sintered at 1350°C and that of 1, 3 and 5 wt% Li_2CO_3 doped BST ceramics sintered at 900°C

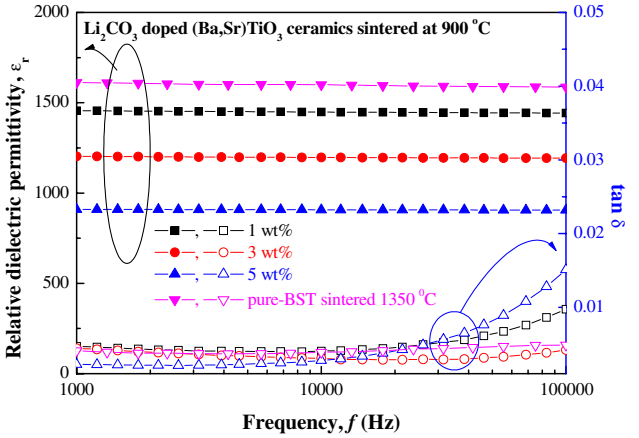

Fig. 2 Frequency dependent relative dielectric permittivity and dielectric loss of 0, 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 1350°C and 900°C, which investigated from 1 to 100 kHz, respectively

3 Results and discussion

Figure 1 shows that the crystalline properties of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 900°C and pure BST ceramic sintered at 1350°C. As shown in the Fig. 1, X-ray diffraction patterns of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 900°C were similar to that of pure BST ceramic sintered at 1350°C. This result means that the Li_2CO_3 doped BST ceramics were crystallized around 900°C. From the X-ray diffraction patterns, we did not find any pyrochlore phase in the Fig. 1 except for the 5 wt.% Li_2CO_3 doped BST ceramic. We found that the pyrochlore phase of 5 wt.% Li_2CO_3 doped BST ceramic is related with the over sintering. From the X-ray diffraction analysis, we found that Li_2CO_3 doped BST ceramics have perovskite structure. The lattice parameters of BST were

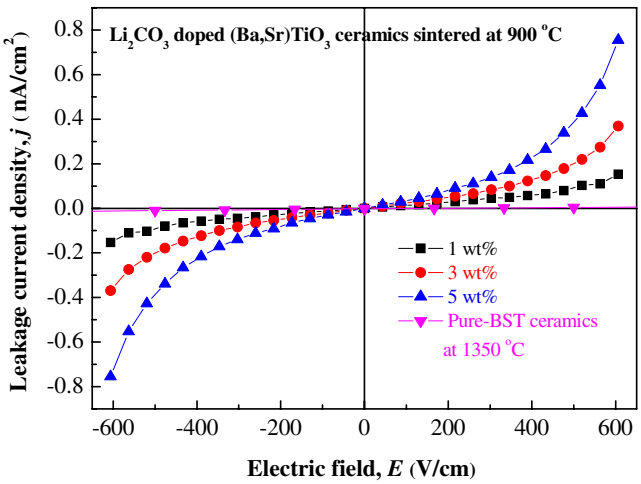

Fig. 3 Leakage current density of 0, 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 1350°C and 900°C, respectively. The electric field was applied from −606 V/cm to +606 V/cm

calculated from the X-ray diffraction analysis. To calculate the lattice parameters of Li_2CO_3 doped BST ceramics, *Nelson-Riley* extrapolation function with least mean square method was employed. The equation can be expressed as follows.

$$\frac{C_{\cos\theta} - C_0}{C_0} = A \cdot \cos^2\theta\left(\frac{1}{\sin\theta} + \frac{1}{\theta}\right) \quad (1)$$

where $C_{\cos\theta}$ is an interplane distance calculated from the apparent Bragg peak position at 2θ and A is a fitting coefficient. From the calculated lattice parameter, the lattice parameters of Li_2CO_3 doped BST ceramics were decreased with the increased amount of Li_2CO_3 and they show the pseudo-cubic states. The calculated lattice parameters of 1, 3 and 5 wt.% of Li_2CO_3 doped BST ceramics were 3.955 Å, 3.951 Å and 3.947 Å, respectively. We found this decreased lattice parameter probably come from the strong chemical bonding energy and the increased density of BST ceramics. The electro negativity of Li, Ba, and Sr were 0.98, 0.89, and 0.95, respectively. The electro negativity of Li was bigger than Ba and Sr. We found that increased Li addition play a role to make more strong bonding with oxygen. In an ideal cubic perovskite ABO_3, the coordination number of the A-site and B-site are 12 and 6, respectively. The ionic radius of Li^+, Ti^{4+}, Ba^{2+}, and Sr^{2+} were 0.76, 0.68, 1.35, and 1.12 Å, respectively. It mean that Li^+ could occupy the A site

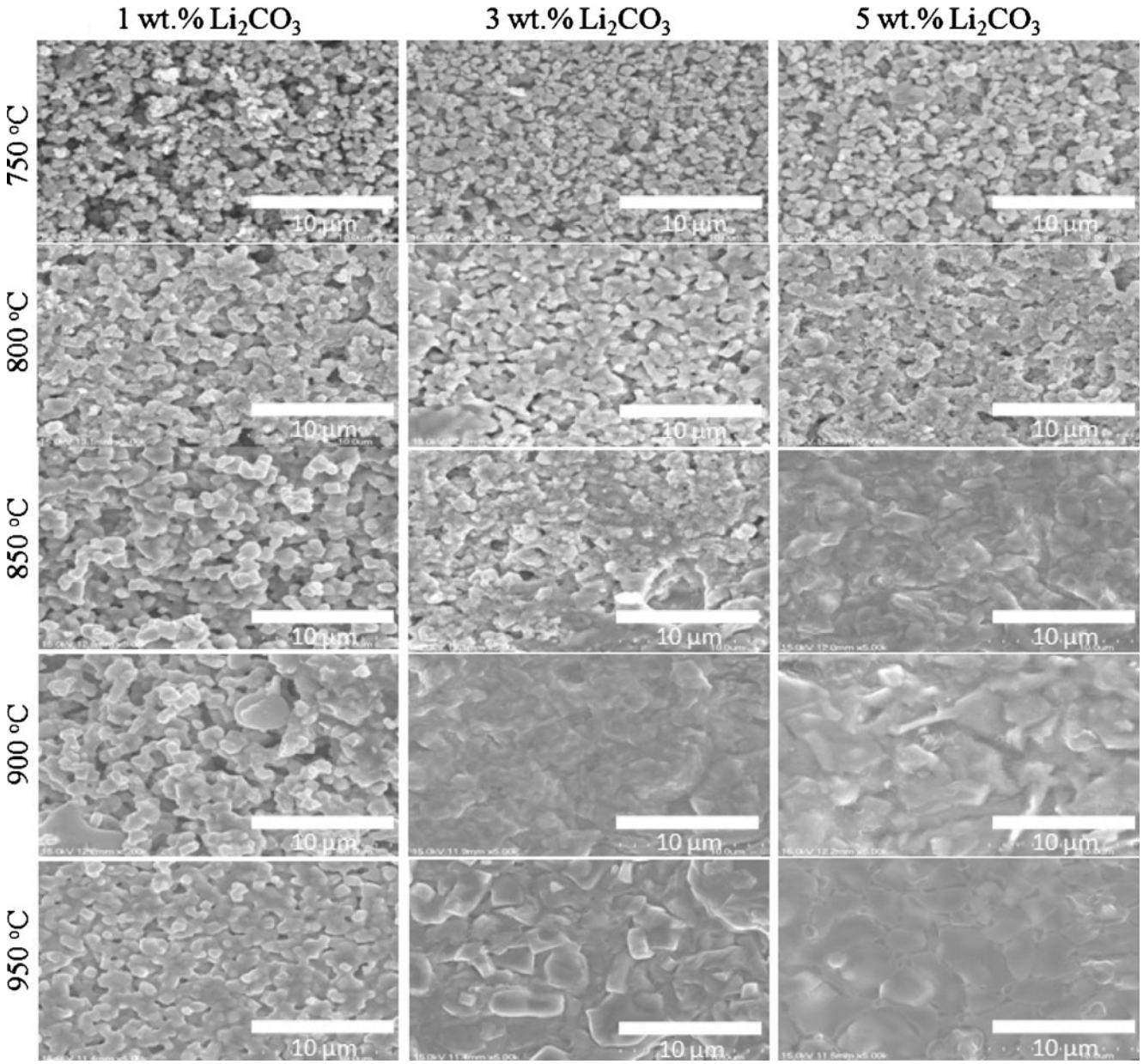

Fig. 4 The microstructure of 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics sintered at various temperatures (white basic bar length: 10 μm)

position than others due to the ionic size of Li^{+} is smaller than ionic size of Ba^{2+} and Sr^{2+} [10, 11]. Therefore, we believe increased bonding energy can be decreased the lattice parameters.

Figure 2 reveals that the frequency dependent relative dielectric permittivity, ε_r' and dielectric loss of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 900°C. Frequency dependent relative dielectric permittivity and dielectric loss were respectively investigated from 1 kHz to 100 kHz range. In this range, each sample shows the weak frequency dispersion of relative dielectric permittivity. In case of 1 wt.% Li_2CO_3 doped BST ceramic, the relative dielectric permittivity was decreased 0.905% with increasing frequency. As shown in the Fig. 2, the relative dielectric permittivity of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics was decreased with the increased amount of Li_2CO_3. The relative dielectric permittivity of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics were 1441, 1194, and 906 at 100 kHz, respectively. Among them, 3 wt.% Li_2CO_3 doped BST ceramic shows the smallest value in this experiment. The dielectric loss of 3 wt.% Li_2CO_3 doped BST ceramic was 0.0042 at 100 kHz. We found that this low loss tangent probably related with the crystal properties and sintering process. Generally, the cubic structure had the low loss tangent than tetragonal structure [12]. Therefore, we found the decreasing loss tangent was related with pseudo-cubic states. However, the 5 wt% Li_2CO_3 doped BST has the high loss tangent than 3 wt% Li_2CO_3 doped BST. We discussed this behavior in the Fig. 4.

Figure 3 indicates that the electric field (E) dependent leakage current density (j) of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 900°C in the electric field of ±606 V/cm range. This leakage current density vs. electric field characteristics measured from the maximum reverse bias, through zero to the maximum forward bias. Ten seconds delay time was employed to reduce the relaxation current. The leakage current density of Li_2CO_3 doped BST ceramics was increased with the amount of dopants. The leakage current density of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics was 0.153, 0.369 and 0.755 nA/cm^2 at electric field of 606 V/cm, respectively. In general, the electrical resistivity of dielectric materials was increased as the density of the dielectric materials was increased. The density of Li_2CO_3 doped BST ceramics was increased with the increased amount of Li_2CO_3 in our experiments. However, increased Li_2CO_3 dopant has influence on ionic conduction properties in the leakage current mechanism [9]. In spite of increasing density, the whole dielectric performances of Li_2CO_3 doped BST ceramics such as relative dielectric permittivity, dielectric loss and electrical properties were degenerated by increasing the amount of Li_2CO_3.

Figure 4 shows the microstructure of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at various temperatures. As shown in the Fig. 4, the grain size of Li_2CO_3 doped BST ceramics was increased with the elevated sintering temperature. Also, the amount of Li_2CO_3 was increased, the density of Li_2CO_3 doped BST ceramics was increased at the same temperatures. Until 800°C, we found the porous ceramics and grains did not revealed necked structure altogether. As increasing the sintering temperature above 800°C, grain in the Li_2CO_3 doped BST ceramic was necked with neighboring grains and then the grain size was increased rapidly. Over the 800°C, necking process of grains happened and grain size was increased with increasing sintering temperature. By introducing the Li_2CO_3 dopant, the sintering temperature was decreased except for the 5 wt.% Li_2CO_3 doped BST ceramic. We found that 5 wt.% Li_2CO_3 doped BST ceramic were over sintered states at 900°C.

Figure 5 displays the electrical resistivity and experimental density of 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at various temperatures. By considering the FE-SEM images and densities of Li_2CO_3 doped BST ceramics, sintered at 900°C, we found that the grains became closed packed (Fig. 4) and the density was increased (Fig. 5). In our experiment, the electrical resistivity of 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 700°C was 33.2, 28.0 and 39.4 GΩ·cm, respectively. Also, the electrical resistivity of 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 750°C was 51.3, 39.9 and 56.2 GΩ·cm, respectively. However, the electrical resistivity of 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics sintered at 900°C was 57.6, 48.8 and 35 GΩ·cm, respectively. As shown in the Fig. 5, the electrical resistivity and experimental density had the maximum value near the 850~900°C, and the electrical resistivity and experimental density decreased with increasing

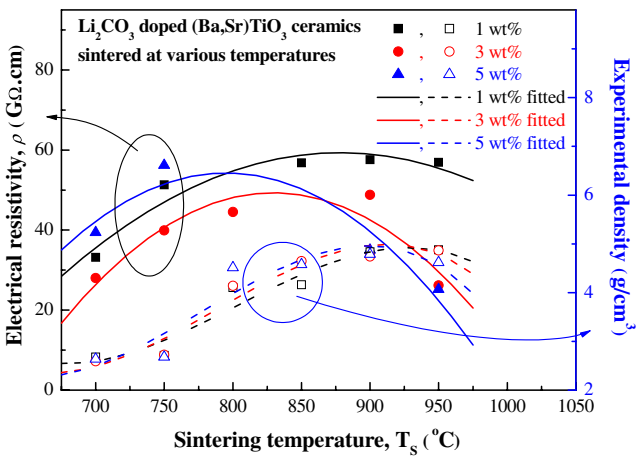

Fig. 5 The variation of electrical resistivity and experimental density of 1, 3 and 5 wt.% Li_2CO_3 doped BST ceramics. Each sample was sintered at various temperatures from 700°C to 950°C, respectively

sintering temperature. Especially, the 5 wt.% doped BST ceramics become over sintered phase above 900°C. Therefore experimental density and resistivity of 5 wt. % doped BST ceramics were degenerated.

4 Conclusions

We fabricated the 1, 3, and 5 wt.% Li_2CO_3 doped BST ceramics sintered at various temperatures. From this experiment, we found that the Li_2CO_3 doped BST ceramics were completely sintered at 900°C. However, we found the pyrochlore phase in the X-ray diffraction pattern of 5 wt.% Li_2CO_3 doped BST ceramic. We found that this unexpected pyrochlore phase was related with the over sintered phase of 5 wt.% Li_2CO_3 doped BST ceramic.

By introducing the Li_2CO_3 dopant to the BST system, the lattice parameters were decreased due to the increased strong chemical bonding energy and increased density. Cubic structure of pure BST, 1 wt% Li_2CO_3 doped BST, and 3 wt % Li_2CO_3 doped BST has the low loss tangent than that of 5 wt% Li_2CO_3 doped BST. This behavior come from the pyrochlore phase, originated from the over sintering property.

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