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Design of $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$-$BaTiO_3$ binary system for MLCC

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In this study, a binary dielectric materials composed of perovskite $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$ and $BaTiO_3$ were designed using conventional solid-state reaction for use in improved dielectric properties of $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$ maintaining the high temperature stability. The experimental results demonstrate that the $80(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3/20BaTiO_3$ shows not only superior dielectric properties (capacitance of 54.9, dielectric loss of 0.13, insulation resistance (IR) value of $1.66E^{+13}$, insulation resistance X capacitance (RC) value of 358,813 at 1 MHz derived from $BaTiO_3$ but also excellent temperature coefficient of capacitance derived from $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$ among various $BaTiO_3/(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$ compositions. It also meets the resistance X capacitance value. $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$ (stable temperature characteristics) and $BaTiO_3$ (high dielectric constant). We suggest that the $80(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3/20BaTiO_3$ can be applied for realizing extraordinary multilayer ceramic capacitors.

Key words: Binary dielectric materials, $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$, $BaTiO_3$, Synergy effect.

Introduction

Multilayer ceramic capacitors (MLCCs) are employed in various information and communication technology (ICT) devices and automotive applications [1]. There are two main dielectric materials for MLCC depending on their purpose. First, $BaTiO_3$ (BT) based ceramics indicating superior dielectric constant can be used as X5R specification (capacitance variation of ± 15% in the temperature range from -55 to 85 °C) [2]. Second, $(Ca_{0.7}Sr_{0.3})(Zr_{0.8}Ti_{0.2})O_3$ (CSZT) based ceramics satisfy the C0G specification (capacitance variation of ± 30 ppm/°C in the temperature range from -55 to 125 °C) with low dielectric loss. Although, CSZT has a low dielectric constant, it has been widely used for high voltage and high frequency applications [3-5].

So far, studies on the aforementioned two materials (CSZT and BT) have been conducted separately. However, the trend of cutting-edge materials research for MLCC requires extraordinary properties such as excellent dielectric properties and temperature stability to apply various applications. Recently, a number of single materials have been investigated to achieve both high dielectric constant and high temperature stability, regardless of their working conditions (voltage, frequency, and temperature). Unfortunately, these approaches are limited by the utilization of a single material. Single material systems cannot meet the needs of the market as a key passive component. Therefore, binary material systems were designed based on the idea of obtaining intermediate properties between high dielectric properties and thermal stability. This is the way to deliver the diverse performance requirements to meet the needs of the customers. Therefore, in this paper, we prepared the CSZT/BT binary dielectric materials for tunable properties and investigated the optimum composition to maximize synergy effect.

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Experimental

CSZT/BT binary materials were fabricated by conventional solid-state reaction, while controlling the ratio of BT and CSZT based slurries. The slurries were prepared using BT and CSZT based powders (Kyriz, Japan) and polyvinyl butyral with ethanol/toluene solvent. The slurry was then ball-milled with zirconia-balls for 24 hrs. Powders also included various additives (MgO (Kojundo chemical, Japan), $BaCO_3$ (Sakai, Japan), DY_2O_3 (Rhodia, China), SiO_2 (Kojundo chemical, Japan), and Mn_3O_4 (Kojundo chemical, Japan)).

The green sheets were prepared through a tape casting method. The sheets were pressed, and then cut into small pieces. They were annealed under 260 °C for 40 hrs in air to remove the polymer binder in the green chips. Then they were sintered at 1500 °C for 4 hrs in a reducing atmosphere to check applicability of MLCC.

Ag paste was applied on both sides of the samples as electrodes and subsequently heat treated at 650 °C for 30 min.

Structural properties of the samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The dielectric properties and the temperature coefficient of capacitance (TCC) values of the samples were measured with an HP 4284A precision LCR meter in a temperature chamber. The insulation resistance (IR) values were measured using a high resistance meter (HP 4329).

Results and Discussion

Fig. 1 shows the XRD patterns of the starting materials CSZT and BT, and CSZT/BT ceramics with different ratio of BT. From the pristine CSZT, the diffraction peaks can be indexed to the (111), (200), (220) and (311), respectively. From the pristine BT, the diffraction peaks can be also indexed to the (100), (110), (111), (211) and (220), respectively. The pristine CSZT and CSZT/BT ceramics shows the CSZT peaks and coexistence of BT and CSZT peaks, indicating that the CSZT/BT binary materials were successfully prepared. All samples were well crystallized without any secondary phase. Main peaks of all samples were strongly affected when the BT content was varied. The intensities of CSZT and BT peaks decreased and increased, respectively, with increase in the BT content. Therefore, we can infer that CSZT/BT ceramics exist as a mixture composed of BT and CSZT, but not as a

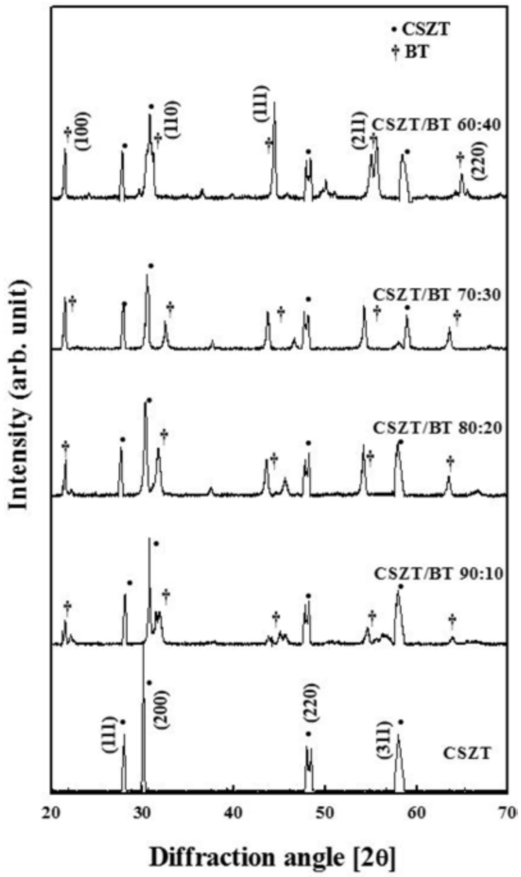

Fig. 1. XRD pattern of pristine CSZT and BT/CSZT ceramics with different BT contents.

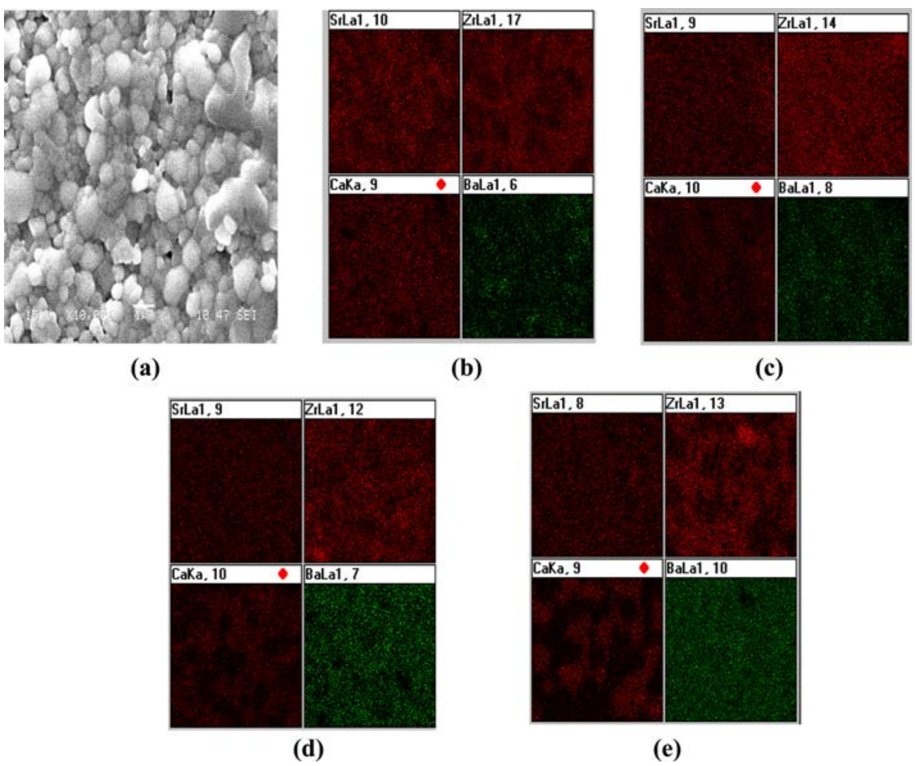

Fig. 2. (a) Microstructure of 20BT/80CSZT ceramics and EDS analysis of (b) 10BT/90CSZT, (c) 20BT/80CSZT, (d) 30BT/70CSZT, and (e) 40BT/60CSZT.

solid solution.

Fig. 2 shows the microstructure of pristine CSZT and CSZT/BT ceramics with different BT ratios. As observed from the SEM image of 80CSZT/20BT in Fig. 2(a), it is difficult to differentiate the BT and CSZT ceramics from each other because of their similar morphologies and average particle sizes (< 1 μm). In order to clearly distinguish them, energy-dispersive X-ray spectroscopy (EDS) analysis was conducted and the results for 90CSZT/10BT, 80CSZT/20BT, 70CSZT/30BT and 60CSZT/40BT are shown in Figs. 2(b-e), respectively. From the EDS results, it can be concluded that all samples were well mixed according to mixing ratios of BT and CSZT. These results are consistent with the XRD patterns presented in Fig. 1. The dielectric and electrical properties can be affected by CSZT/BT binary materials with different BT contents.

The dielectric constants, dielectric losses, IR, and RC values are shown in Fig. 3(a-d). The densities of samples increased with increase in BT contents. Among all the prepared samples, the 80CSZT/20BT system shows the maximum value of density (= 5.28 g/cm^3). Beyond this, those of samples represent reversely tendency to decrease. We can confirm that the dielectric properties exhibited a great consistency with density behaviors. As shown in Fig. 3(a) and 3(b), the dielectric constants were 31.4, 42.9, 54.9, 69.5, and 83.5 for pristine CSZT, 90CSZT/10BT, 80CSZT/20BT, 70CSZT/30BT, and 60CSZT/40BT, respectively. The dielectric losses of the CSZT/BT binary materials were inversely proportional to their dielectric constants. The dielectric losses of pristine CSZT, 90CSZT/10BT, 80CSZT/20BT, 70CSZT/30BT, and 60CSZT/40BT were 0.067, 0.12, 0.13, 0.58 and 0.72, respectively. These results confirm that the dielectric properties of the materials are dependent on their BT contents, with considerable variation in the properties between 20BT and 30BT materials. The IR values, one of the most important factors considered for application in MLCCs, are shown in Fig. 3(c). By transformation from Ti^{4+} to Ti^{3+} ions under both high temperature and reduction atmosphere, the oxygen vacancies of insulating $BaTiO_3$ cause semiconducting behaviors [6]. Oxygen vacancy is considered as a factor that degrades the electrical resistance, which can be explained by the following expression [7-9].

$$BaTiO_3 + xH_2 \rightarrow BaTiO_{3-x}[V_o]_x + xH_2O \quad (1)$$

$$[V_o] \rightarrow [V_o]^{\bullet\bullet} + 2e \quad (2)$$

Where $[V_o]^{\bullet\bullet}$ denotes an oxygen vacancy in the $BaTiO_3$ lattice with an effective charge of +2, according to the Kroger-Vink notation [7]. Ultimately, the oxygen vacancy affects not only IR value but also breakdown voltage of MLCCs that is closely linked with the endurance [10, 11]. Fig. 3(d) shows the RC values of pristine CSZT and CSZT/BT ceramics with different BT ratios. The RC value largely varies with the composition and can have an important impact on the fabrication as MLCCs [12]. We can confirm that the RC value is gradually reduced in proportional to the BT contents. According to the results, the RC values of samples rapidly decreased for BT ratios higher than 20% BT. The 80CSZT/20BT material system has an RC value of 358,813, which indicates that it can be practically used in MLCCs.

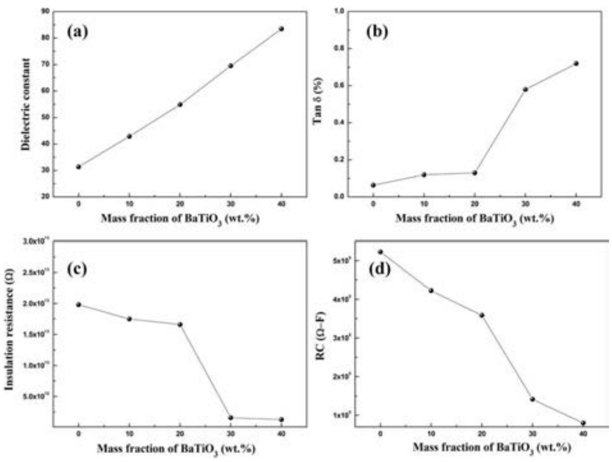

Fig. 3. (a) Dielectric constants; (b) Dielectric loss; (c) Insulation resistance; and (d) RC value of pristine CSZT and BT/CSZT ceramics with different BT ratios.

The most important thing for using C0G MLCC is to meet the temperature characteristics. The TCC of 80CSZT/20BT measured at 1 MHz, in the temperature range from -55 °C to 125 °C is shown in Fig. 4. The dielectric properties of 80CSZT/20BT appear almost constant regardless of the test temperature, which is consistent with that of the pristine CSZT. It can be inferred that although the change in capacitance was naturally increased as the BT contents increase, it still meets the Electronic Industry Association (EIA) specification for C0G dielectric by 20% contents of BT. However, all the CSZT/BT binary materials with BT contents higher than 20% do not meet the C0G specification. This result can be elucidated by inferior temperature stability of BT than that of CSZT.

Conclusions

In this paper, we fabricated (1-x)CSZT-xBT ($0 \leq x \leq 0.4$) binary dielectric materials with different BT contents by conventional solid state synthesis. From the XRD, SEM, and EDS results, we can conclude that all materials were well made, as intended. Among all the prepared samples, the 20BT/80CSZT ceramic exhibited not only extraordinary

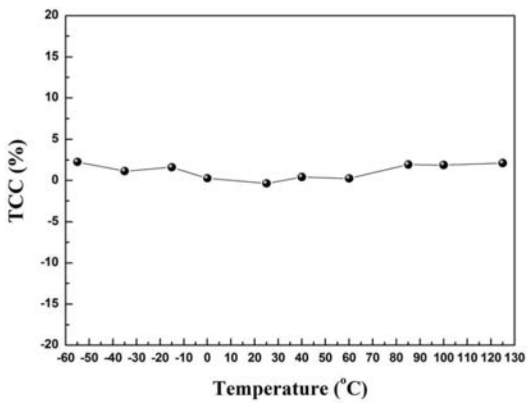

Fig. 4. TCC value of 20BT/80CSZT ceramics in the temperature range from -55 °C to 125 °C.

electrical properties but also high temperature stability. The capacitance, dielectric loss, and IR value of the material were 54.9, 0.13 and $1.66E^{+13}$, respectively at 1 MHz. In addition, it showed a high RC value of 358,813, indicating mass production possibility. Therefore, we can conclude that the 80CSZT/20BT ceramic can be regarded a promising candidate for high performance MLCCs.

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