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Microstructure and dielectric response of (Ba,Sr)TiO_3 filler-dispersed resin composites

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Abstract

Resin-matrix composites dispersing low-loss dielectric ceramic filler have received a considerable interest for high-frequency application, because of their good shape flexibility and controllable dielectric properties. In this study, (Ba,Sr)TiO_3-type ceramic particles have been synthesized by KCl molten salt method to serve as filler particle for resin-matrix dielectric composite. Dielectric measurement confirmed that the composite fabricated by tape-casting demonstrated two times higher dielectric constant of 50.4 than the other composites fabricated by direct-casting using a metal mold. Pore-size distribution as well as ceramic filler content was strongly correlated with the formation of electrical flux in the composites to enhance dielectric constant.

Keywords: Shaping; Porosity; Dielectric properties; $BaTiO_3$ and titanates; Functional applications

1. Introduction

Resin-matrix dielectric composites dispersing low-loss dielectric oxide ceramic filler have received a considerable interest for high-frequency applications such as capacitors, tunable antennas, and other RF devices.[1–3] In general, resin materials show lower dielectric constants (∼5) than oxide ceramics, but resin-matrix composite is possible to demonstrate high dielectric constants based on its ceramic filler and good shape flexibility based on its resin matrix, compared with ceramic monoliths. This composite is also expected to control dielectric constant artificially by adjustment of the ceramic filler content for various device requirements, and therefore it is important to design and engineer its material configuration precisely to match the requests. In particular, antenna modulus working at high operating frequencies requires adjustable dielectric constants as well as shape flexibility which is capable of well-fitting as internal antennas into a minute gap in terminals without no interaction to other electric devices. However, there is only a limited number of reports that dielectric ceramic monoliths show their dielectric constants of 40–80,[4] and this fact is not a small problem for the development of various kinds of directional antennas with the controlled dielectric constant.

In this study, a modified (Ba,Sr)TiO_3 (BST)-type ceramic filler was used as a model composition to prepare resin-matrix composites whose dielectric constant is possible to be tuned, and the relation between their dielectric property and microstructure was investigated from a viewpoint of the effect of residual porosity in composite on the dielectric polarization under applied electric fields.

2. Experimental

$(Ba_xCa_{0.1}Sr_{1-x})(Ti_{0.9}Zr_{0.1})O_3$ ($x = 0.4$–0.8, abbreviated to 10xBCSTZ) was used as a ceramic filler candidate for the preparation of resin-matrix composites. Reagent-grade $BaCO_3$, $CaCO_3$, $SrCO_3$, TiO_2 and ZrO_2 were weighed and mixed in ethanol for 24 h by ball-milling to prepare the nominal compositions of 10xBCSTZ. The dried mixture was calcinated in air at 1150 °C for 2 h, followed by pressing into a disk shape. The pressed sample was sintered in air at 1400 °C for 2 h, then subjected to dielectric measurement to select the best composition with the highest dielectric constant and the lowest dielectric loss at room temperature.

In this test, $(Ba_{0.4}Ca_{0.1}Sr_{0.6})(Ti_{0.9}Zr_{0.1})O_3$ (4BCSTZ) was selected as a ceramic filler composition suitable for resin-matrix

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composites. This filler was then prepared by using a molten salt method, instead of solid-state reaction. The slurry of 4BCSTZ was mixed with KCl in weight ratio of 1:1. The dried mixture was heated at 1250 °C for 2 h, followed by cooling to the room temperature. After this heat-treatment, KCl residue was removed from the product by repeated washing with hot distilled water. The product was dried and sieved to form the ceramic filler powder. The derived powder was then inserted to a container filled with a thermoplastic resin that was kept at 90 °C. The volume ratio of ceramic filler was selected up to 60 vol.% against resin in the mixture. The ceramic/resin slurry was kept stirring for well dispersion before composites were prepared. The resin-matrix composites were formed by two different press-form techniques of a tape-casting (TC) method by using a doctor blade and a direct-casting (DC) method by using a stainless mold under uni-axially pressing.

The crystalline phase and microstructure were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. A laser diffraction particle-size analyzer measured the mean diameter (D_{50}) of the ceramic filler, and a mercury porosimeter characterized the porosity of the composite. The temperature dependence of dielectric property at 100 kHz was evaluated in the temperature range from −40 to 30 °C by using a LCR meter and an environmental chamber. Electric-field distribution in the composites was simulated by finite difference time domain (FDTD) method.

3. Results and discussion

3.1. BCSTZ ceramics

Fig. 1 shows the powder XRD patterns of 10xBCSTZ ceramics. All samples showed a perovskite single phase and no secondary phase, indicating the formation of a solid solution. The every peak shifted toward higher angles with decreasing Ba content (x), since Ba^{2+} (1.56 Å) is larger than Sr^{2+} (1.40 Å) in ionic radius and the d spacing of BCSTZ crystal was reduced by Sr substitution. Accurate lattice parameters of BCSTZ ceramics at room temperature were calculated by the whole-powder-pattern decomposition (WPPD) method.[5] The refined lattice parameters are presented in Fig. 2. The lattice parameters monotonously increase with the increase of Ba content (x). The refinement analysis determined that 4BCSTZ, 5BCSTZ and 6BCSTZ have a cubic symmetry like $SrTiO_3$ structure at room temperature, while 7BCSTZ and 8BCSTZ show a tetragonal symmetry like $BaTiO_3$ structure. The diffractive peaks of (1 0 1) and (1 1 0) planes of the tetragonal symmetry are also shown as a magnified inset in Fig. 1.

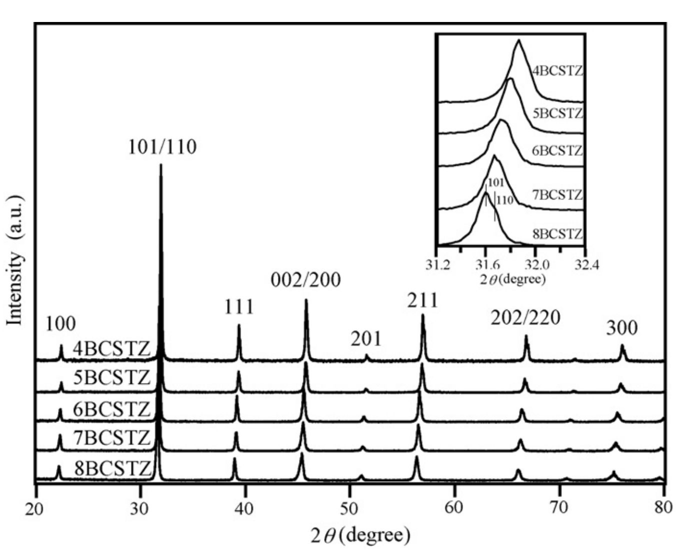

Fig. 1. XRD patterns of $(Ba_xCa_{0.1}Sr_{1-x})(Ti_{0.9}Zr_{0.1})O_3$ ceramics (x = 0.4–0.8, abbreviated to 10xBCSTZ).

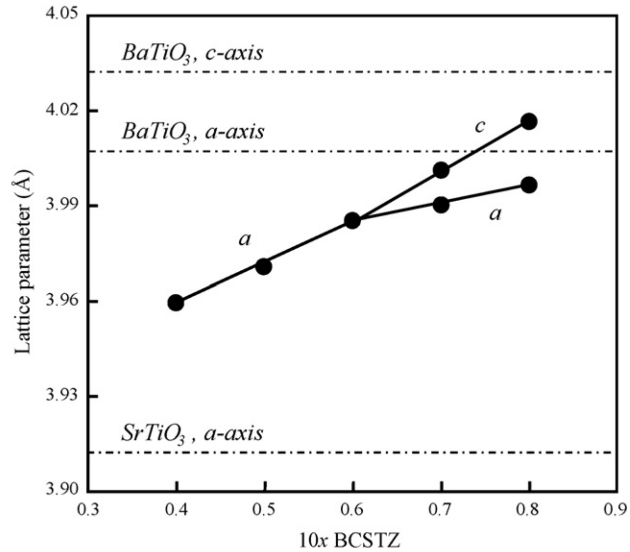

Fig. 2. Refined lattice parameters of BCSTZ ceramics at room temperature.

The temperature dependence of dielectric constant and loss tangent at 100 kHz for 10xBCSTZ ceramics are shown in Fig. 3. The dielectric anomaly corresponding to the phase transformation between tetragonal and cubic was observed at the specific temperature. The temperature of maximum dielectric constant (T_{max}) shifted toward lower with decreasing Ba content (x), and was assigned to be 82 and 58 °C for 8BCSTZT and 7BCSTZT ceramics, respectively. In contrast, 6BCSTZT, 5BCSTZT and 4BCSTZT ceramics did not show obvious T_{max} peaks above room temperature. This tendency was also observed in the measurement of dielectric loss tangent, and also agreed well with the results of phase identification by XRD at room temperature. Of all the candidates, 4BCSTZT was selected as a ceramic filler composition in this study, because of its relatively large dielectric constant and low-loss tangent ($\varepsilon_r = 1700$, $\tan\delta = 3.4 \times 10^{-4}$ at 25 °C) with the minimized temperature variation.

3.2. 4BCSTZ/resin composite

For filler application, a single-phase 4BCSTZ ceramic powder with a mean diameter (D_{50}) of 1.26 μm was obtained by the molten salt method. SEM observation confirmed that the powder had a spherical shape. Fig. 4 shows the variation in the dielectric constant of resin-matrix composite fabricated by DC method as

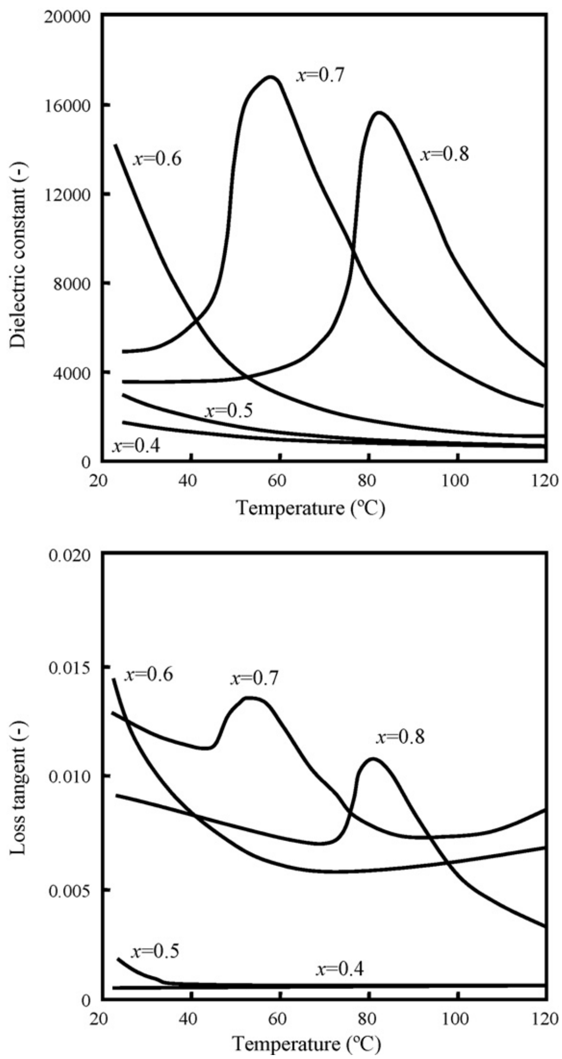

Fig. 3. Temperature dependence of the dielectric constant and loss tangent at 100 kHz for 10xBCSTZ ceramics.

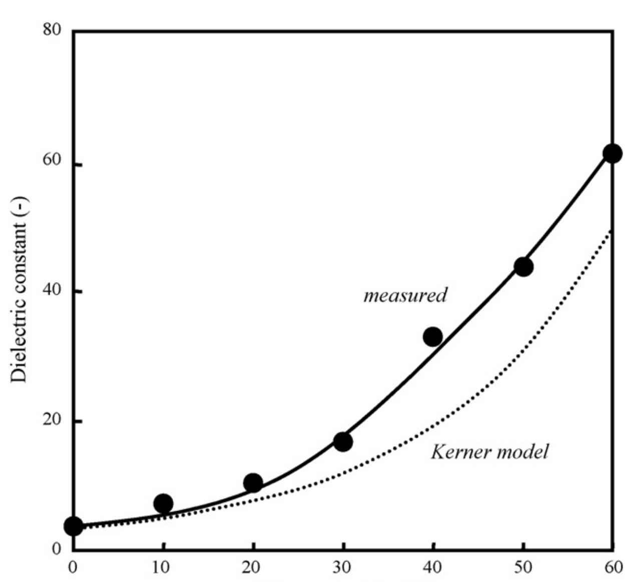

Fig. 4. Variation in the dielectric constant of 4BCSTZ/resin composite fabricated by DC method as a function of the filler content.

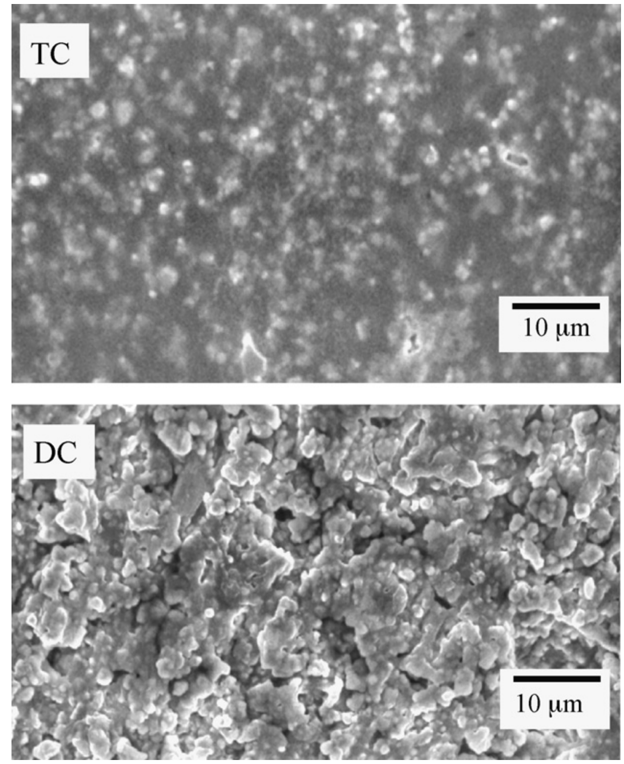

Fig. 5. SEM micrographs of the 4BCSTZ (40 vol.%)/resin composites fabricated by TC and DC methods.

a function of the filler content of 4BCSTZ ceramics. This figure also plots the dielectric constant predicted by the following Kerner model for comparison[6]:

$$\varepsilon = \frac{\varepsilon_1 v_1 + \varepsilon_2 v_2 \left[3\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)\right] \times \left[1 + 3v_2(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)\right]}{v_1 + v_2 \left[3\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)\right] \times \left[1 + 3v_2(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)\right]} \qquad (1)$$

where ε, ε_1 and ε_2 are dielectric constant of composite, resin matrix (=3) and ceramic filler (=1700), respectively, and v_1 and v_2 represent the volume fractions of resin matrix and ceramic filler. This Kerner model is a rule-of-mixture model used for dielectrics and is often utilized to predict the dielectric constant of 0–3 type composites in case where it is assumed that small particles disperse well in matrix material and set their positions in parallel and vertical configurations against uni-directional electrical fields. It can be confirmed that the dielectric constant measured in 4BCSTZ/resin composite comparatively agrees well with the results estimated by Eq. (1) in the filler content ranging from 10 to 30 vol.%. On the other hand, higher dielectric constants were measured in comparison to the predicted value for the composites having filler contents over 40 vol.%. Unlike the Kerner model, the effect of aggregation (bulk effect) of the filler particles might appear in this result.

Fig. 5 shows the SEM micrographs of the two different resin-matrix composites with 4BCSTZ ceramic filler of 40 vol.%. These two composites showed a similar apparent density of 2.72 g/cm^3 (DC method) and 2.68 g/cm^3 (TC method), and total porosity of 16.2% (DC method) and 18.5% (TC method). However, the composites fabricated by DC method obviously contained large pores with their size of 10 μm or more. On the other hand, small pores with their size less than 1 μm, which is nearly equivalent to the size of ceramic filler particle, occupied the microstructure of the composites fabricated by TC method contained. It seems that air was easily trapped into the composite when the pressing was performed, because air could not be escaped outward from the mold in their forming step. In contrast, the composite fabricated by TC method contained almost no large pore, because the sheer stress induced by moving of a doctor blade dominated and large pores were reduced to small pores and eliminated from the composite during forming process. The difference in pore-size distribution between two specimens affected their dielectric constants significantly.

Fig. 6 presents the temperature dependence of dielectric constant measured for two different composites fabricated by TC and DC methods. The dielectric constant at 0 °C for the composites fabricated by TC and DC methods was 54.4 and 29.3, respectively. The dielectric constant of the composite fabricated by TC method showed nearly twice value than that of the composite fabricated by DC method, although loss tangent was in the same order of 10^{-3} for both composites in the temperature range measured. It is generally accepted that the dielectric constant of ceramics is changeable by inner stress during processing.[7] In the present study, however, pressing stress was induced mostly to the resin matrix (low ε_1), because resin is mechanically soft compared with ceramic powder (high ε_2). Therefore, the observed difference in the dielectric constant

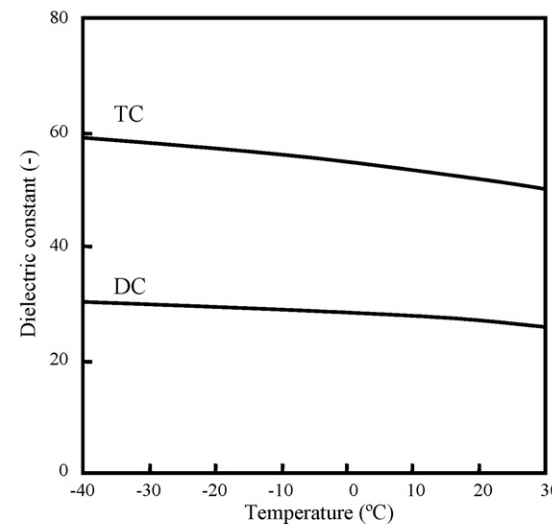

Fig. 6. Temperature dependence of the dielectric constant measured for two different 4BCSTZ (40 vol.%)/resin composites fabricated by TC and DC methods.

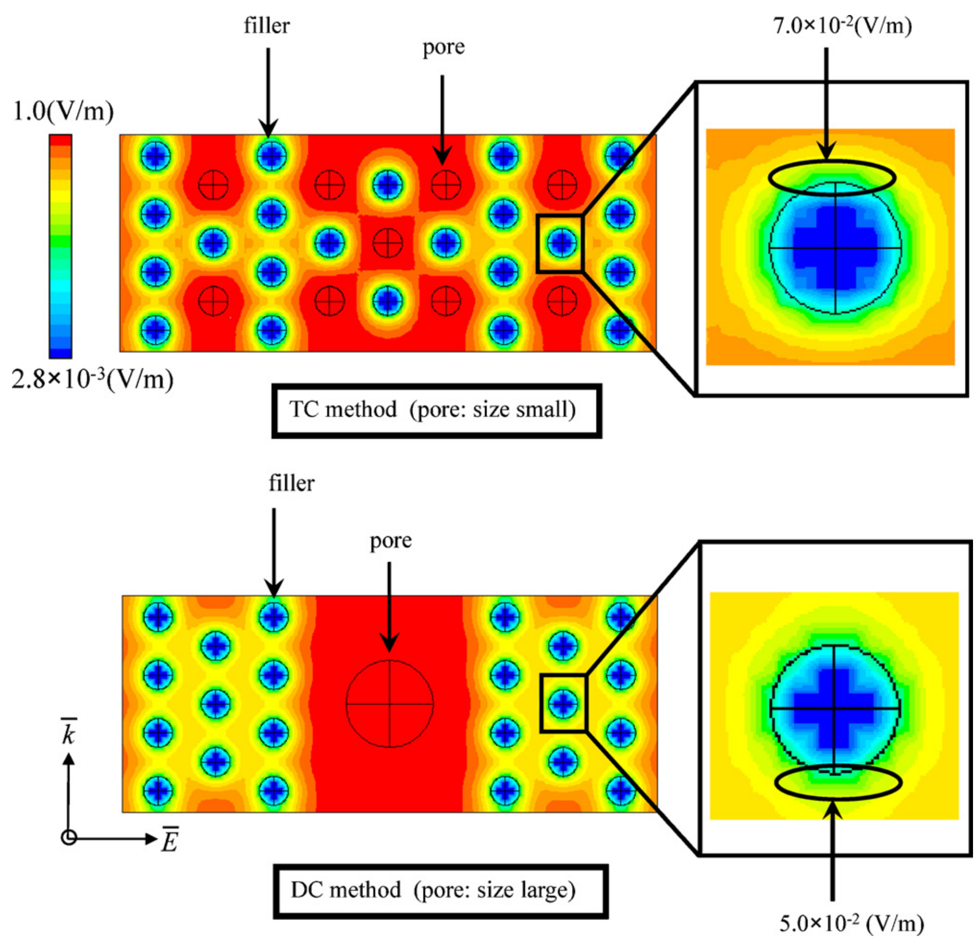

Fig. 7. Calculated near electric field using FDTD method for 4BCSTZ (40 vol.%)/resin composites fabricated by TC and DC methods.

between two different specimens seems to have been closely correlated with porosity rather than the residual stress. It is considered that local large pores received a concentrated electric field and prevented from applying electric field to ceramic filler, since pore is filled with air showing dielectric constant of approximately 1. As a result, only a limited dielectric polarization in ceramic fillers seems to have worked to enhance the dielectric constant of the resin-matrix composite derived from DC method. In other words, the dielectric constant of resin-based composite is attributable to the degree of the effective electric field developed in ceramic filler particles surrounded by pores.

To elucidate this behavior, electromagnetic wave simulation was carried out using FDTD method. The results are shown in Fig. 7. For this simulation, we designed the unit cell composed of a square dielectric where the ceramic filler and the pore, with different diameters but the identical total volume, were embedded inside the resin-matrix. In this figure, both x and z axes are rectangular periodical directions, and the incident wave number k is in the other y direction. The simulated intensity of the near electric field in the z plane of the two different resin-based composites can be compared in Fig. 7. Electric-field intensity of the surface of ceramic filler particle was calculated to 5.0×10^{-2} V/m in the composite where large pores in comparison with the diameter of the ceramic particle was embedded. On the other hand, the electric-field intensity was increased up to 7.0×10^{-2} V/m (40% up) for the composite where small pores equivalent to the ceramic particle in diameter distribute in the composite homogeneously. The former and latter cases assume the composite fabricated by DC and TC methods, respectively. Therefore, an increase in the stored electric energy at the surface of ceramic particle seems to have enhanced the dielectric polarization of ceramic filler in case where large pore was eliminated by tape-casting method.

4. Conclusion

In this study, $(Ba_{0.4}Ca_{0.1}Sr_{0.8})(Ti_{0.9}Zr_{0.1})O_3$ (4BCSTZ) ceramics was selected as a ceramic composition suitable for fabricating resin-matrix composites dispersing low-loss dielectric ceramic filler, and higher dielectric constant was obtained in the 4BCSTZ/resin composite fabricated by tape-casting method to reduce pore size by using sheer stress during the forming process. It was likely that the dielectric constant of resin-based composite was determined by the degree of the effective electric field developed in ceramic filler particles surrounded by pores. Therefore, elimination of large pore and well dispersion of ceramic filler particle are of importance to engineer good dielectric behavior of resin-matrix composite.

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