Paraelectric ceramics/metal dual composites $SrTiO_3/Pt$ system with giant relative permittivity

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Dielectric properties of $SrTiO_3$–Pt (platinum) composites prepared using conventional ceramic method were investigated. Dense complex ceramics were obtained without chemical reaction between $SrTiO_3$ and Pt during sintering processes. The relative permittivity (ε_r) of $SrTiO_3$ was increased by the addition of Pt particles nearly up to the percolation threshold of 27.8 vol % as predicted using normalized percolation theory. The maximum ε_r of 2150 at 1 MHz was obtained for the composite including 27 vol % Pt due to the increased electric field around Pt particles. Using finite difference time domain method, the increase of electric field in the direction of applied electric field was confirmed visually in the vicinity of the embedded metal particles. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2361176]

Paraelectric ceramics have been used widely as an important component of dielectric resonators for communicative microwave applications because of their low dielectric loss relative to ferroelectric ceramics.[1–3] In particular, paraelectric ceramics with a high permittivity (ε_r) are useful for miniaturization of dielectric resonators, antennas, and other devices. Furthermore, it might be possible for paraelectric ceramics with a giant ε_r to replace the ferroelectric ceramics as passive components in capacitors, because it is attractive that the paraelectric materials show no phase transition in a wide temperature range. In general, formations of solid solutions, texture engineering and mixing rules[4] have been used to obtain high ε_r. For instance, Ohsato has reported a scientific approach for enhanced ε_r in the $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solution, where R represents rare earth.[5] According to that report, the ε_r depends on the (1) volume of TiO_6 octahedra, (2) tilting of the octahedral string, and (3) polarizability of R cations. Furthermore, Wada *et al.* enhanced the dielectric properties through texture engineering.[6] They also succeeded in enhancing ε_r for $Ba_4Sm_{9.33}Ti_{18}O_{54}$ dielectric ceramics. However, these methods are insufficient to obtain enhancement of ε_r by a factor of several times.

On the other hand, a system composed of an electric conductor and an insulator phase is known to show a high value of ε_r.[7–9] Recently, Pecharroman and Moya has reported that ferroelectric $BaTiO_3$ with giant ε_r was obtained through the addition of Ni particles to utilize a percolative phenomenon whereby the electric field inside the matrix was enhanced microscopically.[10] This result suggests that a complex material composed of paraelectric ceramics and metal powder is useful for fabrication of paraelectric ceramics with giant ε_r.

In this study, we report dielectric properties of $SrTiO_3$ (ST)-Pt composites as a function of Pt contents and compare the variation of ε_r in measurements with those predicted theoretically using the normalized percolation theory. We chose ST as a paraelectric matrix phase because of its high ε_r (=300), which is suitable for preparing composites with giant ε_r. Electromagnetic (EM) wave simulation results are also demonstrated using finite difference time domain (FDTD) method to elucidate the variation of the electric field intensity inside dielectric ceramics that include metal particles.

The ST-Pt composites were prepared using the following conventional ceramic method. As starting materials, $SrCO_3$ (99.5%), TiO_3 (99.97%), and Pt (99.9%) powders were used. The $SrCO_3$ and TiO_2 were weighed according to the stoichiometry of ST. Then they were mixed for 24 h in ethanol with zirconium balls. After drying, the powder mixture was calcined at 1050 °C for 18 h. The calcined powder was mixed with Pt powders in ethanol using a mortar and pestle for 1 h to form the ST-xPt, where x=5, 15, 25, 26, 27, and 30 vol %. After drying, a binder (polyvinyl alcohol) was added to the powders. The granulated powder was pressed into a cylindrical shape under uniaxial pressure of 7.84 MPa, followed by cold isostatic pressing at 200 MPa. The prepared pellets were sintered at 1300 °C for 2 h in air. Silver electrodes were pasted on both sides of the pellets.

X-ray power diffraction (XRD) was used for phase identification (Philips X'Pert MPD, Kanagawa, Japan). The apparent density of the samples was measured using the Archimedes method. Results showed values higher than 92% for all samples. The dielectric properties of the samples were measured using an impedance analyzer (Agilent 4294A, Kobe, Japan). The EM wave simulations were performed using FDTD method.

Figure 1 shows XRD patterns of the ST-xPt ceramics (where x=0 and 25 vol %) that had been sintered at 1300 °C for 2 h. Because ST (Ref. 11: short bars) and Pt (Ref. 12: long bars) have the same structure (simple cubic) and closed lattice parameters of 3.905 and 3.923 Å, respectively, each XRD peak is similar in 2θ position except of their intensity. The 2θ position of the maximum peak of ST-xPt ceramics was changed from 32.39° to 39.79° with the addition of Pt. The 39.79° corresponds to the 2θ position of the maximum peak of Pt. In addition, no secondary phase was observed in the XRD patterns, indicating that no chemical reaction occurred between ST and Pt during sintering processes.

Frequency dependence of the real part of permittivity (ε_r) with the addition of Pt is shown in Fig. 2. No notewor-

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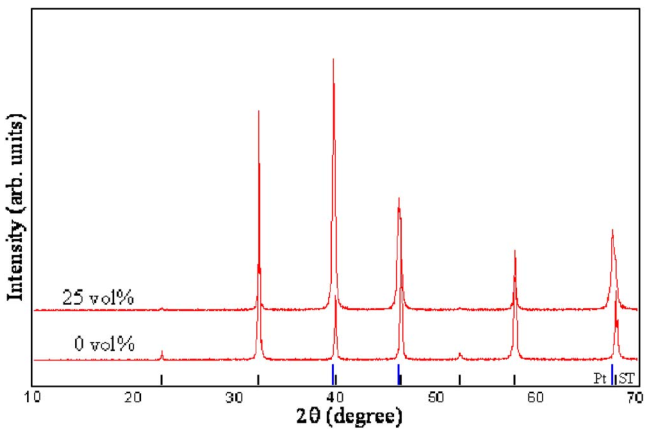

FIG. 1. (Color online) Powder XRD patterns of ST and ST-25 vol % Pt sintered at 1300 °C for 2 h. The short and long bars at the bottom of XRD patterns, respectively, represent ST and PT peaks according to the ICDD cards.

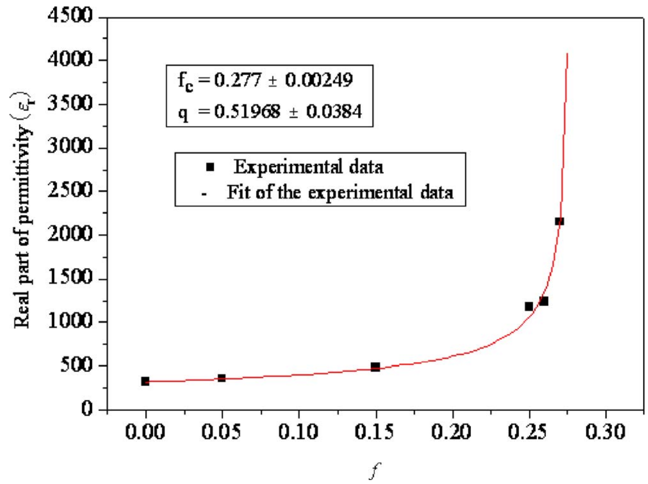

FIG. 3. (Color online) Real part of permittivity (ε_r) of ST as a function of Pt. The solid line represents the fit of experimental data (symbol) according to the normalized percolation theory.

thy dielectric dispersion was observed in the measured frequency range, except for the ST-30 vol % Pt sample, which was not measured because of its conductive behavior. The ε_r increased from 316 to 2150 at 1 MHz with the increased amount of Pt from 0 to 27 vol %. In particular, we observed a considerable increase of ε_r in the narrow range from 26 to 27 vol % Pt. A similar behavior was observed in the neighborhood of the percolation threshold in a conductor-insulator composite.[13]

To calculate the percolation threshold for the present case, we used the normalized percolation theory as in the following equation:

$$\varepsilon = \varepsilon_{\mathrm{ST}}\left(\frac{f_c - f}{f_c}\right)^{-q}, \tag{1}$$

where ε is the dielectric constant of composites, $\varepsilon_{\mathrm{ST}}$ is the dielectric constant of ST, f is the filling factor, f_c is the percolation threshold, and q is a critical exponent.

The theoretical curve fitted using Eq. (1) is shown in Fig. 3. The fitting parameters were $\varepsilon_{\mathrm{ST}}=316$, $f_c=0.277$, and $q=0.519$. These f_c and q were, respectively, close to the theoretical predictions of 0.33 and 0.76–0.89,[14,15] suggesting that the ST-Pt system has a uniform microstructure without any irregular distribution. Furthermore, Eq. (1) might imply that higher ε_r than 2150 is obtainable at the closest percolation threshold over 27 vol % Pt.

The increase in ε_r is attributable to the effective electric field developed between the dispersed Pt particles in the matrix. To further elucidate this behavior, EM wave simulation was carried out using FDTD method. For the simulation, we designed the unit cell as composed of a square dielectric with $\varepsilon_r=316$ ($1\times3\times1$ mm^3) and three metal particles (perfect electric conductor) with different diameters embedded inside the dielectric, where both x and z directions are periodical, and the incident wave number k is in the y direction (as shown in Fig. 4). The simulated intensity of the near electric field in the z plane, at 1 MHz, of insulator-conductor systems is shown in Fig. 4, which represents (a) a dielectric only and (b) a dielectric with metal particles. We observed that the electric field intensity near the embedded metal particles was increased along the direction of the applied electric field (x direction), in comparison with dielectric materials including no metal particles. The increase of the stored electric energy (W_e) inside the dielectric caused by strong refractions/reflections of the metals is expressed as

$$W_e = \frac{1}{4}\,\mathrm{Re}\int_V \vec{E}\cdot\vec{D}^{*}dV, \tag{2}$$

where $\vec{E}$ is the electric field intensity and $\vec{D}$ is the electric flux density. The increased stored electric energy can

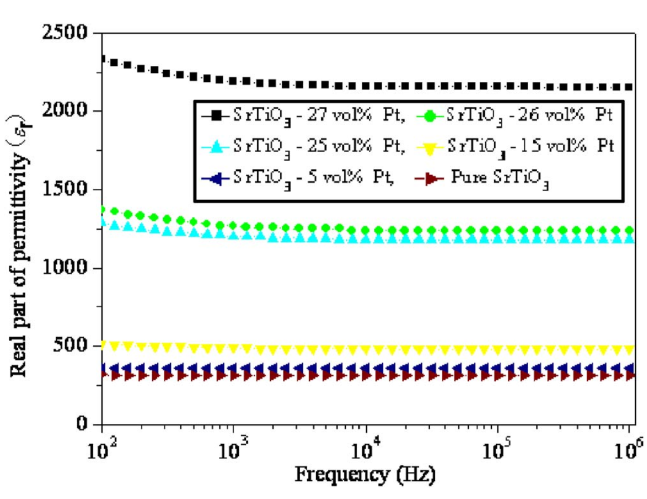

FIG. 2. (Color online) Frequency dependence of real part of permittivity (ε_r) of ST with the addition of Pt.

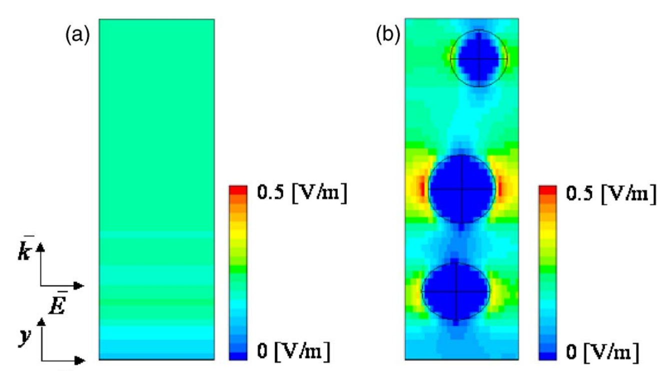

FIG. 4. (Color online) Calculated near electric field using FDTD method at 1 MHz of (a) dielectric only and (b) dielectric with metal particles of different diameters.

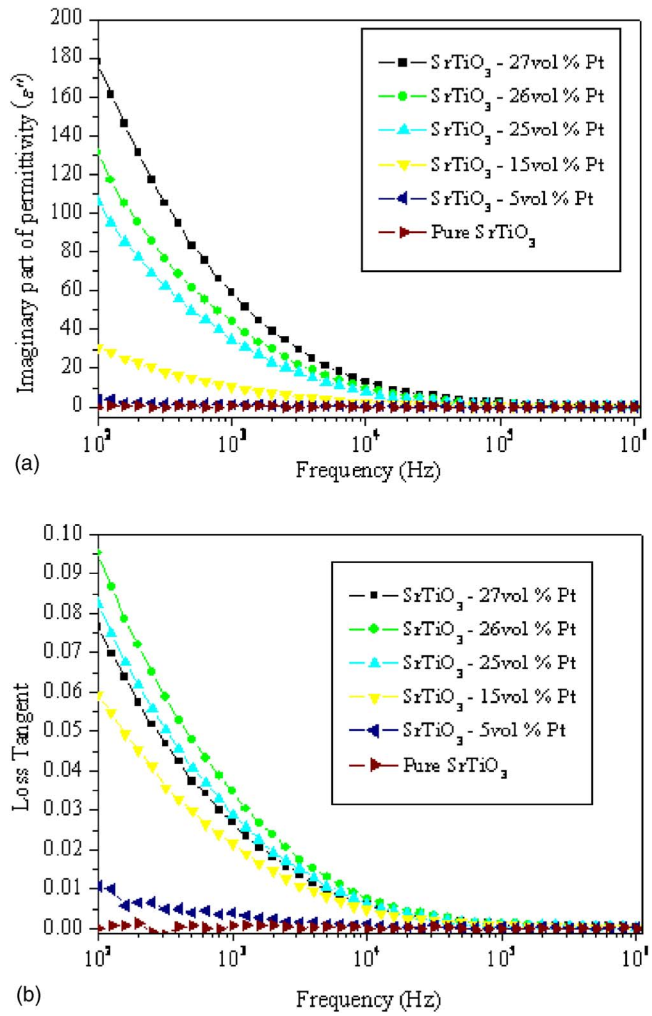

FIG. 5. (Color online) Frequency dependence of (a) imaginary part of permittivity (ε'') and (b) loss tangent with the addition of Pt.

strongly affect the increase in ε_r. Simulation results verify that the electric field intensity depends on the direction of the applied electric field, which can help to elucidate anisotropic behavior such as BN–SiC composites[16] that show an anisotropic property in ε_r depending on the direction of applied electric field, because BN has a platelet structure. Moreover, its stored electric energy is distributed differently inside the microstructure.

Figures 5(a) and 5(b) show the frequency dependence of the imaginary part of permittivity (ε'') and the loss tangent with the addition of Pt, respectively. The value of ε'' increased markedly as an increasing amount of Pt in the low frequency range. However, ε'' decreased with increased frequency, which can be understood by the expression $\varepsilon''=\sigma(f)/\omega\varepsilon_0$. Interesting results are shown in Fig. 5(b): even though the ST-27 vol % Pt composite exhibited the highest ε'' [in Fig. 5(a)], the loss tangent of the composite was lower than the ST-25 and ST-26 vol % Pt composites, meaning that an exponential increase in ε_r near the percolation threshold decreases the loss tangent as expressed by $\tan\delta=\varepsilon''/\varepsilon_r$.

In summary, for fabrication of paraelectric ceramics with giant ε_r, the dielectric properties of ST including different contents of Pt particles have been measured and analyzed using normalized percolation theory and FDTD method. During the sintering process, Pt did not react with ST. Increased ε_r of ST was observed as increasing the amounts of Pt particles, a giant ε_r of 2150 at 1 MHz was obtained for the composite of ST-27 vol % Pt, which is close to the percolation threshold of 27.8 vol %, as predicted by the normalized percolation theory. Using FDTD method, we observed the increased intensity of the electric field in the neighborhood of metal particles along the direction of the applied electric field, which increased ε_r. The ε'' also increased with an increasing amount of Pt; however, it decreased with increasing frequency. Development of paraelectric ceramics with giant ε_r is quite useful for the miniaturization of electronic components in capacitors and other devices.

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