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Frequency dependence of dielectric properties of metallodielectric $SrTiO_3$–Pt composites

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Abstract

The frequency dependence of dielectric properties of $SrTiO_3$–Pt (platinum) composites has been investigated. The $SrTiO_3$–Pt composites sintered at 1300 °C for 2 h was prepared by using conventional ceramic fabrication method. The dense metallodielectric composites without chemical reaction between $SrTiO_3$ and Pt during sintering process were obtained. The relative permittivity (ε_r) of $SrTiO_3$–Pt composites was increased with increase of amount of Pt. The maximum ε_r of 2150 at 1 MHz was obtained for the composite of $SrTiO_3$–27 vol.% Pt. Moreover, the $SrTiO_3$–Pt composites exhibited high values of ε_r at low frequencies than at high frequencies due to space charge polarization. The loss tangent ($\tan\delta$) of $SrTiO_3$–Pt composites increased with increasing amount of Pt, and decreased with increasing frequency up to 1 MHz. However, the $\tan\delta$ of $SrTiO_3$–Pt composites was significantly increased at microwave frequency due to abrupt increase of ac conductivity of composite.

Keyword: Dielectric properties

1. Introduction

Paraelectric ceramics have been playing as key components of dielectric resonator for microwave communication application in the microwave circuits because of their low dielectric loss relative to ferroelectric.[1] In particular, paraelectric ceramics with high permittivity (ε_r) are useful for miniaturization of electronic components such as dielectric resonator, antennas, and other devices. Moreover, It is expected that paraelectric ceramics with giant ε_r should be useful candidate as passive components in capacitors instead of ferroelectric due to no phase transition. In order to obtain high ε_r, many methods have been reported such as formations of solid solution, texture engineering and mixing rule.[2–4] However, by these methods it was difficult to enhance ε_r of paraeletric ceramics by a factor of several times.

On the other hand, percolative phenomenon is a useful method to achieve a high ε_r. In general, the behavior occurs in materials filled with inclusions such as highly conducting fibers distributed randomly in a host, which demonstrates a insulator–metal transition with increasing metal concentration.[5–7] According to percolation theory, the electric properties such as ε_r, electrical conductivity changes significantly with composition when one phase in the mixture is approaching its percolation threshold.[8] Recently, ferroelectric $BaTiO_3$ with giant ε_r has been reported by Pecharroman et al. which used percolative phenomena where the microscopic average electric field inside matrix is increased.[9] However, to the best of our knowledge, there are no reports of paraelectric with giant ε_r. To fabricate a paraelectric with giant ε_r, we choose paraelectric $SrTiO_3$ (ST) as host material due to its advantages of relatively high ε_r.

In this study, the sintering properties of $SrTiO_3$–Pt dual composites are investigated. In addition, the frequency independence of dielectric properties and conductivity of ST–Pt composites as a function of Pt particle concentration is presented.

2. Experimental procedures

Reagent-grade $SrCO_3$ (99.5%), TiO_2 (99.97%) and Pt (99.9%) were used as raw materials. To prepare strontium titanate ceramic $SrTiO_3$, $SrCO_3$ and TiO_2 were mixed according to the stoichiometry of $SrTiO_3$ in an ethanol with zirconia balls for 24 h. After drying, the powder mixture was calcined at

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1050 °C for 18 h. The calcined $SrTiO_3$ powder again mixed with Pt powders in a motar with ethanol and pestle for 1h according to the composites of the $SrTiO_3$–xPt, where $x = 5$, 15, 25, 26 and 27 vol.%. Subsequent to above process, polyvinyl alcohol was added to the reground powder. The powder was pressed into cylindrical shape under a uni-axial pressure of 7.84 MPa and then was again subjected to cold isostatic pressing (CIP) at a pressure of 200 MPa. The prepared pellets were sintered at 1300 °C for 2 h in air. Then sliver electrodes were pasted on both the side of the pellets for measurement of impedance analyzer.

The microstructures of the sintered samples were observed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The crystalline phase of the sintered samples were characterized by X-ray power diffraction (XRD) using Cu Kα radiation (Philips X'Pert MPD, Kanagawa, Japan). The bulk density was determined by the Archimedes method. The dielectric properties and ac conductivity of the samples up to 1 MHz were measured by using an impedance analyzer. In addition, the microwave dielectric properties were measured by the modified Hakki and Coleman's method in the TE_{011}[10,11] mode using a network analyzer.

3. Results and discussion

The XRD patterns of the SrTiO–xPt composites (where $x = 0$, 15 and 25 vol.%) sintered at 1300 °C for 2 h are shown in Fig. 1. The patterns of both $SrTiO_3$ and $SrTiO_3$–Pt composites agree very well with ICDD card 79-0174 ($SrTiO_3$: short stick) and 70-2057 (Pt: long stick), respectively. The intensity of $SrTiO_3$ is decreased with increase of amount of Pt. The maximum XRD peak was changing from 32.39° (maximum XRD peak of ST) to 39.79° (maximum XRD peak of Pt) with increase of Pt. In addition, secondary phases were not observed in the XRD patterns. This suggests that chemical reaction has not occurred between ST and Pt during the sintering process.

Fig. 2 shows the measured density of $SrTiO_3$–Pt composites. The apparent density of $SrTiO_3$–Pt composites increased with increasing amount of Pt. This is because Pt (21.461 g/cm^3) has a higher a theoretical density than $SrTiO_3$ (5.118 g/cm^3). On the other hand, the relative density of one decreased with increasing amount of Pt.

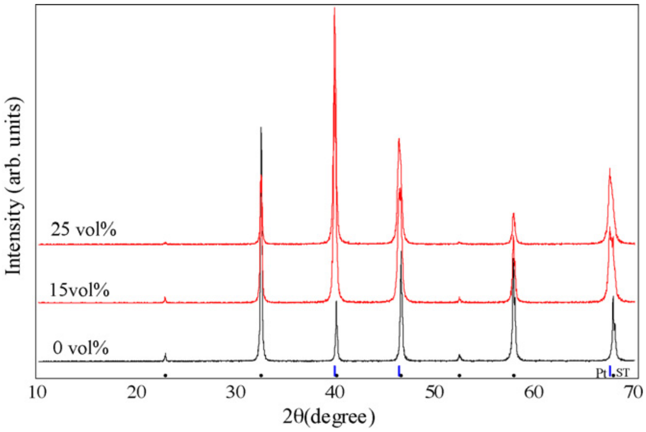

Fig. 1. X-ray diffraction patterns of $SrTiO_3$–xPt composites sintered at 1300 °C for 2 h: (a) $x = 0$, (b) $x = 0.15$ and (c) $x = 0.25$. The short and long sticks at the bottom of XRD patterns represent ST and Pt peaks according to the ICCD cards, respectively.

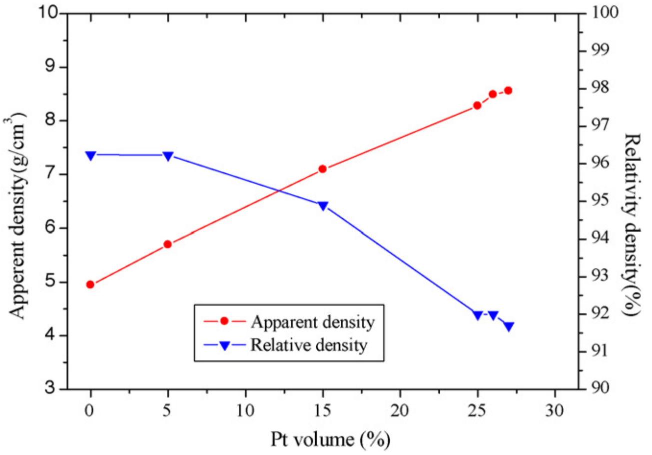

Fig. 2. Apparent and relative density of $SrTiO_3$–Pt composites sintered at 1300 °C for 2 h.

The SEM images of composites with different volumes of Pt and their EDS image are shown in Fig. 3. It is seen in Fig. 3(b)–(d) that light gray particles are uniformly distributed on the surface of matrix. Fig. 3(e) represents the region framed in Fig. 3(d) at a higher magnification, showing that the light gray particles which was identified as Pt by EDS analysis (Fig. 3(f)). In addition, the Pt agglomerated with increasing amount of Pt. The coalescence of Pt may be caused by pores. These pores also contributes to the decrease of relative density of $SrTiO_3$–Pt composites with increasing amount of Pt.

Fig. 4 shows the frequency dependence of ε_r of the $SrTiO_3$–Pt composites. The ε_r of $SrTiO_3$–Pt composites increased with increasing amount of Pt. The $SrTiO_3$–27 vol.% Pt composite exhibited maximum value ε_r of 2150 at 1 MHz. The ε_r of $SrTiO_3$–Pt shows a high value at low frequency compared with one at high frequency due to space charge polarization, which occurs at interfaces of two materials with different conductivity. In addition, in the range of low frequency from 100 Hz to 1 kHz, the $SrTiO_3$ with high Pt concentrations exhibit relatively high dielectric dispersion with frequency compared with the $SrTiO_3$ with low Pt concentrations because of large amount of space charge polarization.

The frequency dependence of loss tangent ($\tan\delta$) of $SrTiO_3$–Pt composites are shown in Fig. 5. The $\tan\delta$ of $SrTiO_3$–Pt composites increased with increasing amount of Pt. It shows high $\tan\delta$ at lower frequencies due to space charge polarization. As increasing frequency up to 1 MHz, the $\tan\delta$ of one rapidly decreased since space charge polarization does not affect significantly a $\tan\delta$ in the range of high frequency. Also, it can be interpreted as following the expression:

$$\varepsilon''(f) = \frac{\sigma(f)}{\omega\varepsilon_0} \tag{1}$$

where ε'' is the imaginary part of permittivity, σ the conductivity of composite, and ω (=2πf) is the angular frequency. According

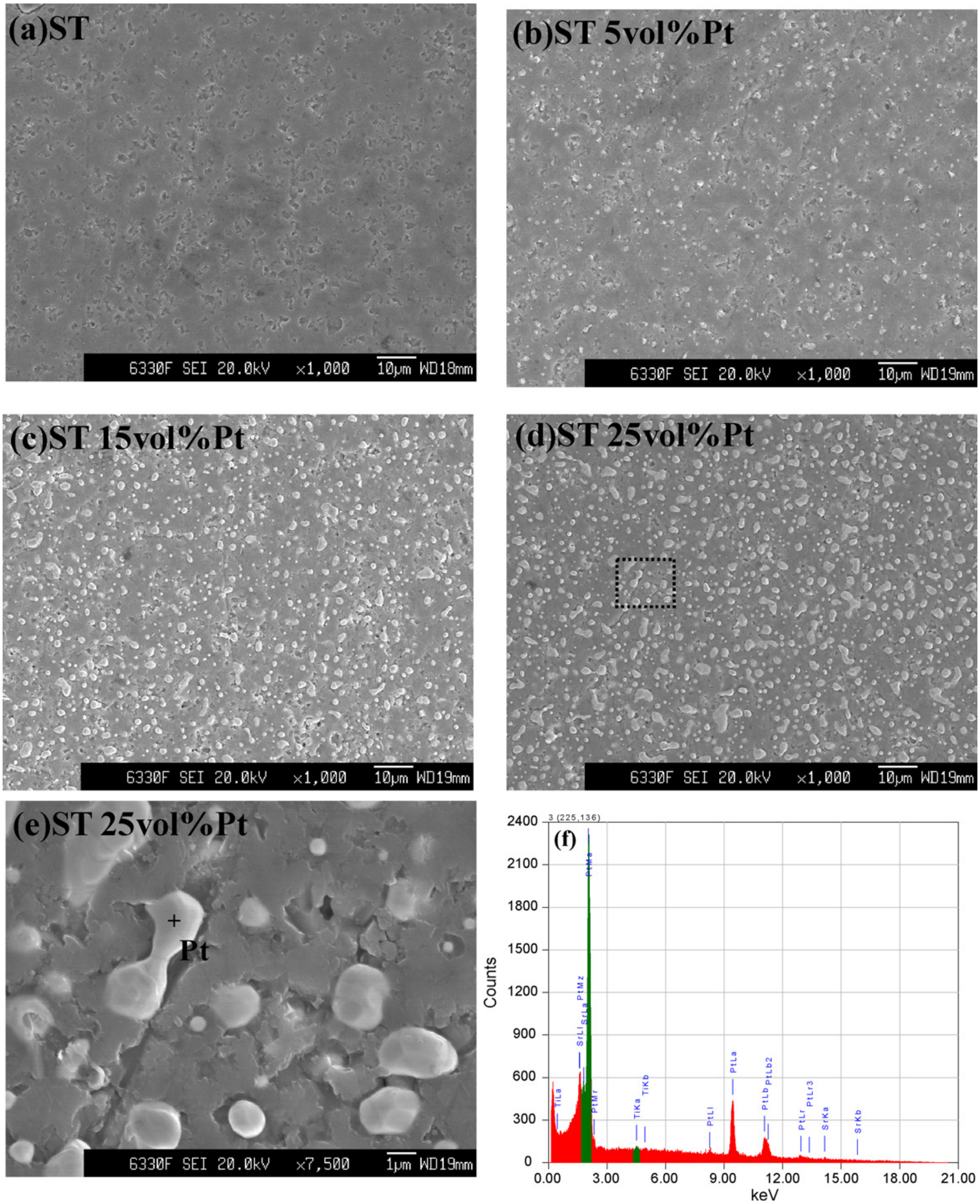

Fig. 3. SEM images of $SrTiO_3$–xPt composites sintered at 13:00 h for 2 h: (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.15$, (d) $x = 0.25$, and (e and f) enlarged SEM image and EDS spectra of $x = 0.25$.

to Eq. (1), ε'' is decreased as increasing frequency. On the other hands, the tan δ of one at microwave shows again a high tan δ, which is observed in composites with high Pt concentration more clearly. It can be expected that such significant increase of tan δ at microwave results from the increase of $\sigma(f)$. In order to verify the behavior, we measured the ac conductivity of $SrTiO_3$–Pt composites.

The measured ac conductivity of $SrTiO_3$–Pt composites is shown in Fig. 6. The ac conductivity of $SrTiO_3$–Pt composites increased with increasing amount of Pt as well as the increase of frequency. Particularly, the variation rate of the ac conductivity with frequency at above 100 kHz is higher than one in the range of low frequency. Although, the ac conductivity of $SrTiO_3$–Pt composites at microwave could not measure in this study, large increase of ac conductivity can be expected in the microwave range. Such exponential increase of ac conductivity with increasing frequency affects a high tan δ at microwave.

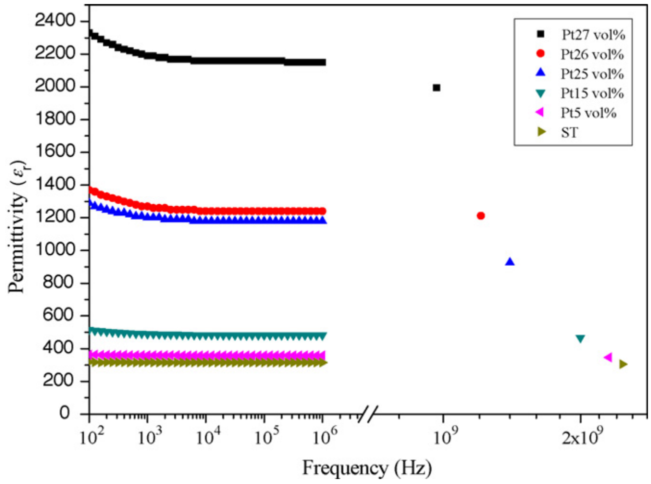

Fig. 4. Frequency dependence of real part of permittivity (ε_r) of $SrTiO_3$–Pt composites.

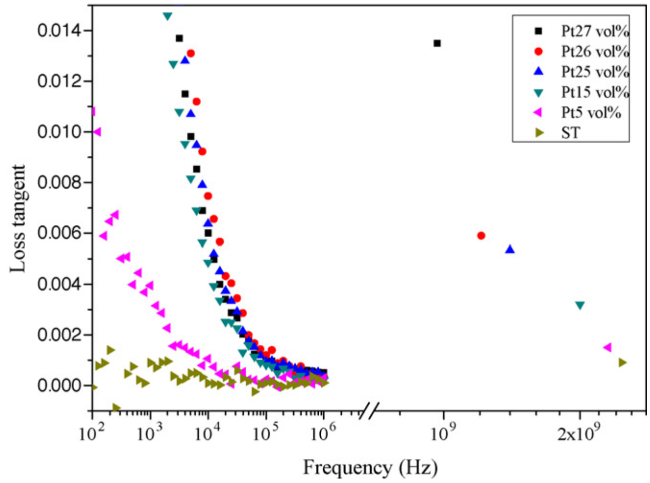

Fig. 5. Frequency dependence of loss tangent of $SrTiO_3$–Pt composites.

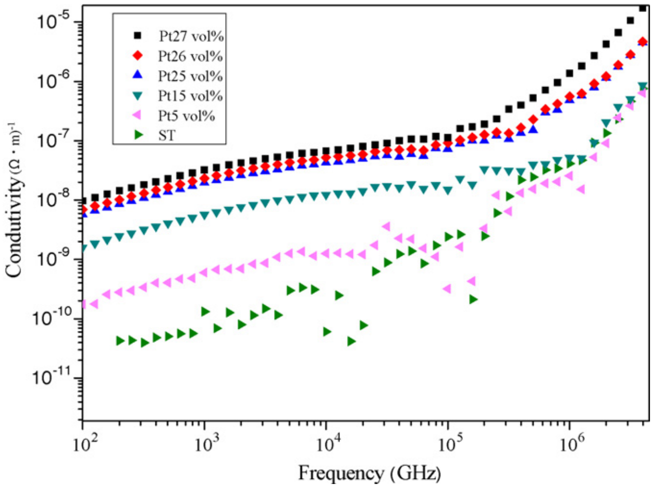

Fig. 6. Frequency dependence of conductivity of $SrTiO_3$–Pt composites.

4. Conclusion

The dielectric properties of $SrTiO_3$–Pt dual composites with frequency have been investigated. The dense $SrTiO_3$–Pt composites sintered at 1300 °C for 2 h, without chemical reaction between $SrTiO_3$ and Pt during sintering process, were obtained. The ε_r and $\tan\delta$ were increased with increase of amount of Pt. The $SrTiO_3$–Pt composites exhibit high dielectric dispersion and high $\tan\delta$ in low frequency areas due to the amount of large space charge polarization. On the other hand, the $\tan\delta$ of $SrTiO_3$–Pt composites were decreased with increasing frequency up to 1 MHz, and then it was significantly increased at microwave possibly because of exponential increase of ac conductivity.

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