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Dielectric Behavior of $Na_{0.5}Bi_{0.5}TiO_3$-Based Composites Incorporating Silver Particles

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The dielectric properties of $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) -based composites incorporating silver particles prepared by sintering at a low temperature of ~900°C are reported. The dielectric constant increases with the amount of metal silver particles in the measured frequency range (150 Hz to 1 MHz), and could be enhanced up to ~20 times higher than that of pure NBT ceramics, which was ascribed to the effective electric fields developed between the dispersed particles in the matrix and the percolation effect. Further investigation revealed that the dielectric constant of the composites has weak frequency and temperature dependence (−50°C to +50°C).

I. Introduction

With the miniaturization and integration of electronic circuits, some devices based on capacitive components with high dielectric constant, low loss tangent, and good physical and chemical stability will ultimately decide the degree of miniaturization.[1,2] Usually, high dielectric constants are found in ferroelectric perovskite oxides such as lead zirconate-titanate (PZT) and ferroelectric-based relaxor oxides ($PbMg_{1/3}Nb_{2/3}O_3$; PMN),[3,4] which have been applied in many fields. However, all perovskite materials show strong temperature-dependence of their dielectric constants, and most such perovskites contain lead. Boundary layer capacitors (BLC) based on semiconducting perovskites such as $SrTiO_3$ have also been attractive.[5,6] These capacitors are normally processed in a reducing or partial oxidizing atmosphere so that the grains of the ceramics become semiconducting, whereas the grain boundaries are insulating. However, these capacitors are of poor reproducibility and complex processing and exhibit a strong variation in electrical properties with temperature and frequency, which limits their applications. Creation of lead-free materials with a high static dielectric constant and good stability over wide temperature and frequency ranges is highly desired.[7] Most recently, the lead-free perovskitelike oxide $CaCu_3Ti_4O_{12}$,[8] and Li-, Ti-co-doped NiO ceramics[9] have been reported to possess extraordinarily high static dielectric constant near room temperature, comparable to those for PZT or PMN.

Alternatively, the effective dielectric constant of a metal-insulator mixture, based on the percolation theory, could be much larger than that of a single component dielectric and increase by several orders of magnitude. Such composites have recently attracted much attention.[10–12] Pecharroman *et al.*[13] have reported $Ni/BaTiO_3$ composites with very high dielectric constants, but the metal/ceramics composites still need to be sintered at a high temperature of ~1300°C, and oxidation of nickel must be prevented.

In this paper, we report a $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)–Ag composite prepared by a simple powder-processing route at low-temperature (900°C) in air. NBT-based ceramics are excellent candidates for piezoelectric, pyroelectric, and electro-optic applications. Some studies[14,15] of NBT have focused on the peculiarities accompanying the phase transition, dielectric, ferroelectric, and optical properties. NBT is ferroelectric at room temperature with a diffuse-phase transition. Two phase transformations of interest are the cubic-to-tetragonal (paraelectric state to antiferroelectric state) and tetragonal-to-rhombohedral (antiferroelectric state to ferroelectric state) phase transitions. The dielectric constant (ε) of pure NBT is ~240 at 1 kHz, dielectric loss ($\tan\delta$) is ~1.2%, piezoelectric charge coefficient (d_{33}) is ~50 pC/N, and remanent polarization (P_r) is 38 $\mu C/cm^2$.[16] Appropriate cation modification in NBT, e.g., K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}, can influence both the phase transitions and the dielectric and ferroelectric properties. Our NBT–Ag composite exhibits a high dielectric constant near room temperature of ~5000, shows weak temperature dependence of the dielectric constant over a wide temperature range from −50°C to +50°C, and weak frequency dependence in the frequency of 150 Hz to 1 MHz.

II. Experimental Procedures

Na_2CO_3, Bi_2O_3, TiO_2, $AgNO_3$ were used as raw materials. First, pure $Na_{0.5}Bi_{0.5}TiO_3$ ceramic powders were synthesized at 950°C for 2 h by conventional solid-state reaction. The calcined NBT powder and $AgNO_3$ powder were mixed thoroughly by ball-milling for 24 h. The resultant NBT–Ag precursor powders were pressed into green pellets of 10 mm in diameter and ~1.4–2.0 mm in thickness at a pressure of 10 MPa using polyvinyl alcohol as a binder. The pellets were finally sintered at a low temperature of ~900°C for 2 h in air.

The relative density was measured by the Archimedes method. X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDX) were used to reveal the microstructure and phase composition of the NBT–Ag composites.

Sintered samples were polished and electrodes were made by painting silver paste on both sides of the disk-shape samples and firing at 600°C for 30 min. The dielectric behavior was measured with an impedance analyzer (Model HP4194A, Hewlett Packard, Palo Alto, CA) in the frequency range from 150 Hz–1 MHz at a bias voltage of 1.0 V.

III. Results and Discussion

XRD patterns of the NBT–xAg samples with x = 0, 5, 10, 15, and 20 vol%, (Fig. 1) indicate that no detectable impure phase appears besides NBT and silver. The relative intensity of the

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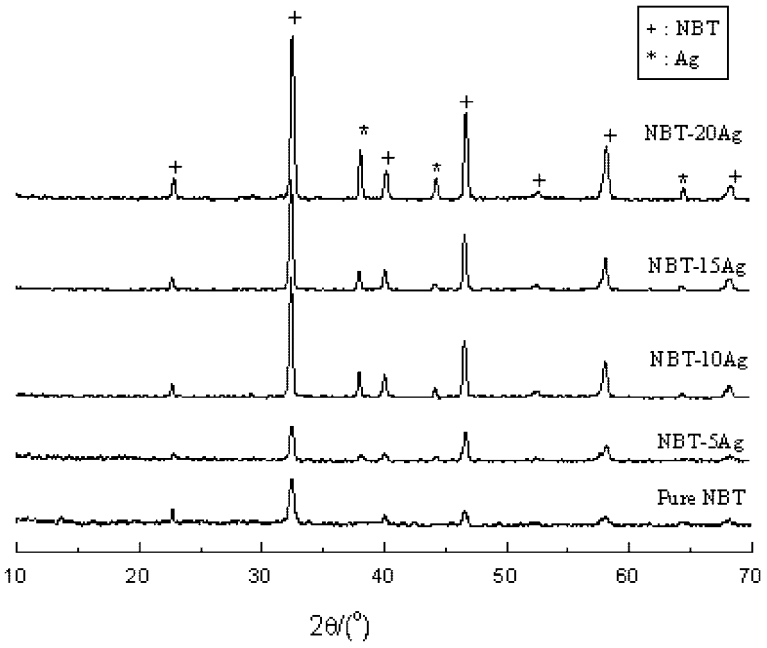

Fig. 1. XRD patterns of different NBT–Ag samples sintered at 900°C for 2 h.

characteristic peaks of the silver phase increases with the volume fraction of silver. The addition of silver greatly lowers the sintering temperature by ~250°–300°C compared with the sintering temperature (1150°–1200°C) for pure NBT.[17,18] This may be because of the softening of the silver particles with a low melting point (~953°C). As reported previously,[19,20] silver can act as an effective sintering aid for PZT and $SrBi_2Nb_2O_9$ ceramics. Therefore, the addition of silver to NBT makes it possible to sinter the NBT–Ag ceramic composites at low temperature.

Figures 2(a) and (b) show SEM micrographs of the as-fired and fracture surface of the NBT–15Ag composite sintered at 900°C for 2 h. The results reveal that dense NBT–Ag composites can be obtained; the relative density of the NBT–10Ag composite ceramics reaches 95%. EDX analysis results (Figs. 2(c) and (d)) indicate that only the Ag phase exists in selected area 1 and only NBT phase exists in selected area 2. The silver particles are dispersed in the NBT matrix, especially in the grain-boundary region. No reaction phases between NBT and silver are observed, in good agreement with the results of XRD analysis.

Figure 3 shows the dielectric behavior measured for the NBT–*x*Ag composites. As seen, these composite ceramics exhibit a weak frequency dependence of the dielectric behavior; however, when the silver concentration is 20%, a decrease in the dielectric constant appears at high frequency, and accordingly, the dielectric

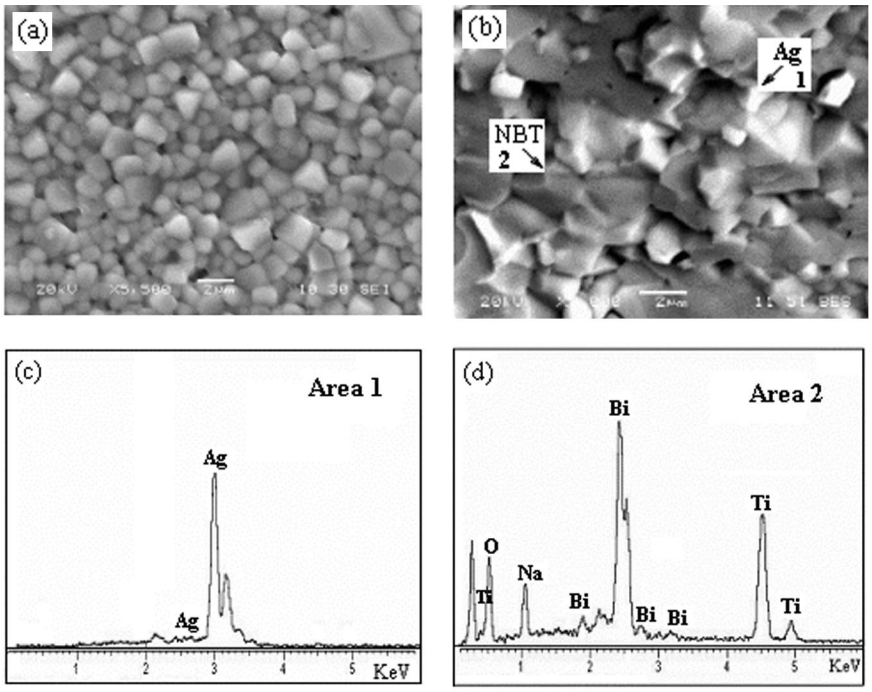

Fig. 2. SEM micrographs of (a) as-fired and (b) fracture surface of the NBT–15Ag sample sintered at 900°C for 2 h. EDX spectra of (c) selected area 1 and (d) area 2 marked in (b).

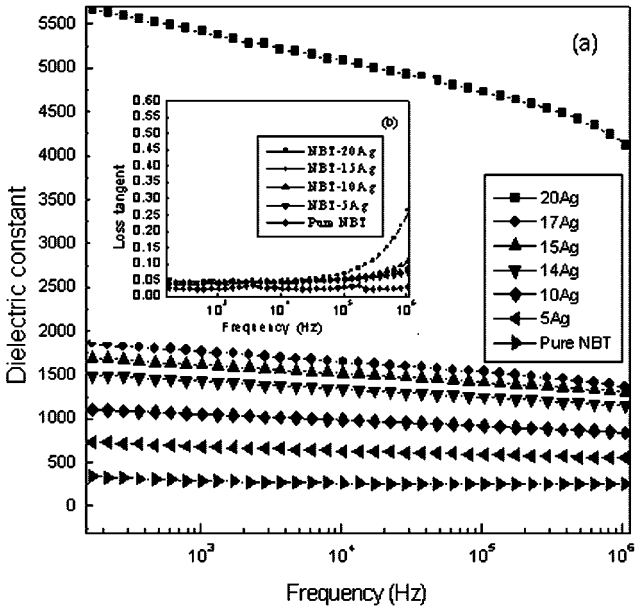

Fig. 3. Frequency dependence of (a) the dielectric constant and (b) loss tangent of the NBT-*x*Ag composites.

loss increases. The similar dielectric behavior has been reported in the Ni/$BaTiO_3$ system by Pecharroman and his co-workers.[13] Actually, the dielectric properties of these metal-insulating composites are also influenced by the grain size, internal stress, metal/oxide interface, and so on.[21] We believe this behavior is associated primarily with interfacial relaxation at high concentrations of silver. As the silver volume fraction is low, the silver particles are dispersed into the NBT ceramic matrix, and thus the dielectric behavior of the composites is dominated by the NBT ceramic matrix. With increasing the silver volume fraction, the silver particles form large particle clusters and even continuous clusters, and thus interfacial relaxation becomes obvious. Similar phenomena have been observed in the composites of epoxy resin with copper or iron particles, $SrBi_2Nb_2O_9$–Ag composites.[22,23]

It is interesting to note the variation of the dielectric constant with the silver volume fraction. As shown in Fig. 4, the dielectric constant of the NBT–*x*Ag composite ceramics increases with *x*. For example, the dielectric constant of the NBT–20Ag composite is ~20 times higher than that of the pure NBT ceramic. Normally, the incorporation of nonferroelectric secondary phase reduces the dielectric constant of ferroelectric materials.[24] Nevertheless, the dielectric constant of the NBT–Ag composites exhibits a gradual increase with increasing volume fraction of silver. It is known that the effective electric fields developed around the conducting phase result in an increase in the dielectric constant of composites.

Some researchers have described the dielectric behavior of the composite system with a conducting phase dispersed in an insulating matrix, such as PZT–Ag and PZT–Pt.[25,26] The dielectric behavior of such a metal-dielectric composite can be well described by the percolation theory.[10,27] The dielectric constants of the NBT–Ag composites can be enhanced further by addition of metallic particles. As seen from Fig. 4(a), usually only a small right rise in the dielectric constant is noticed unless the metallic particle concentration is very close to the percolation point. This is because the variation of the effective dielectric constant in the neighborhood of the percolation threshold can be given by the following power law:[28]

$$\varepsilon \propto (f_c - f_{Ag})^{-s} \tag{1}$$

where ϵ is the dielectric constant of NBT–Ag composites, f_{Ag} is the volume fraction of the metallic silver particles, [f_c] is its percolation threshold, and *s* is a critical exponent.

A best fit of Eq. (1) to our experimental data near the percolation threshold is performed as shown in Fig. 4(b). The results indicate that the experimental values of the dielectric constant are in good agreement with Eq. (1), with $f_c \approx 0.21$ and $s \approx 1$. Such a large increase in the dielectric constant is caused by the existence of a large number of metal particles in parallel and in very close proximity, but blocked by thin barriers of the dielectric material.

The variation of the dielectric constant with temperature for the NBT–*x*Ag composites is shown in Fig. 5. Only a relatively modest increase in the dielectric constant can be observed over the measured temperature range from −50° to +50°C. High dielectric constant and thermal stability of NBT-based ceramics incorporating metallic silver particles potentially make such composite ceramics attractive for capacitors with high-charge density.

IV. Conclusions

Dielectric ceramic-metal NBT–Ag composites have been successfully fabricated at low sintering temperature, and no chemical reaction between two phases has been detected. The dielectric

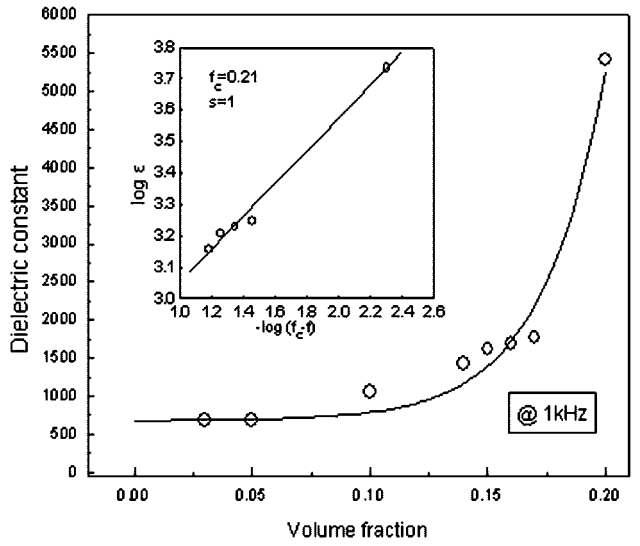

Fig. 4. Dielectric constant of NBT–*x*Ag composites as a function of volume fraction of silver with logarithmic plot of Eq. (1).

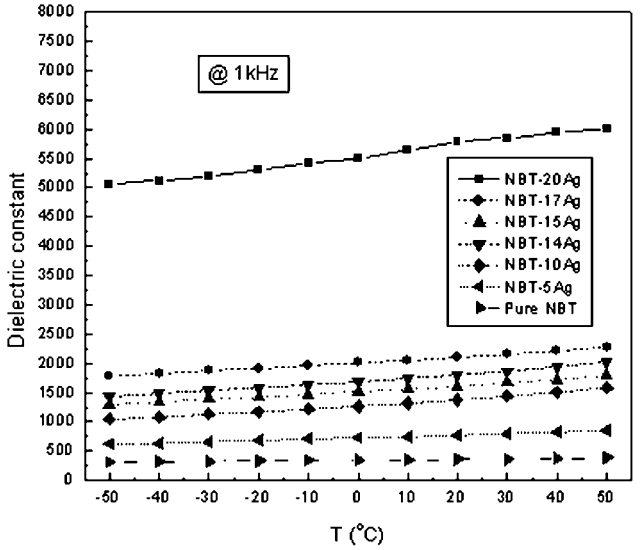

Fig. 5. Variation of the dielectric constant of the NBT–*x*Ag composites with temperature.

properties of the composites have been greatly enhanced by dispersing silver metal particles dispersed in the NBT ceramic matrix. The dielectric constant of the composites has weak frequency (150 Hz to 1 MHz) and temperature (−50°C to +50°C) dependence. Further investigations are needed to fully understand the effect and mechanism of silver doping on dielectric properties of NBT ceramics.

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