

Curie Temperature Anomaly in Lead Zirconate Titanate/Silver Composites

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The Curie temperatures of lead zirconate titanate-based (PZT-based) composites that were incorporated with silver particles were evaluated as a function of the silver content. Although the substitution of the silver ion has been considered to decrease the Curie temperature, PZT/silver composites exhibited higher Curie temperatures than those of monolithic PZT ceramics. It was found that the Curie temperature gradually increased as the silver content increased. It was suggested that the observed Curie temperature anomaly resulted from the relaxation of transformation-induced internal stress by intergranular silver particles.

I. Introduction

THERE are several possible mechanisms that are responsible for the shift of the Curie temperature of perovskite-type compounds ($A^{2+}B^{4+}O_3$); these mechanisms include (i) the substitution of foreign ions into the A^{2+} - or B^{4+} -sites of a crystal structure¹⁻⁴ and (ii) external pressure.⁵⁻⁷ The Curie temperature shifting via the first mechanism is explained by the modification of the unit-cell size, which is caused by the introduction of the foreign ions that have different ionic radii. If the unit cell is shrunk or expanded via the application of hydrostatic pressure or two-dimensional pressure, the Curie temperature also shifts for the same reason.

In addition to these mechanisms, the Curie temperature is dependent on the microstructure of polycrystalline ferroelectrics.^{8,9} Hiroshima *et al.*⁸ systematically investigated the effect of microstructure on the Curie temperature in lead barium niobate solid solutions. These researchers discussed the shift of the Curie temperature in terms of internal stress, which results from the tetragonal deformation of each of the grains under the ferroelectric phase transformation. Smaller grain sizes (larger grain-boundary area) and lower relative density (pore density) reduce the internal stress, and, as a consequence, the Curie temperature shifts to a higher temperature.

Furthermore, it is also expected that, not only the grain size and relative density but also the secondary dispersoids (e.g., soft metal particles) that are dispersed in the matrix, can lead to modification of the Curie temperature of ferroelectric materials. This phenomenon can occur because the strain energy produced by the stresses will be generally relieved by soft grain-boundary phases.

In our previous paper,¹⁰ $Pb(Zr,Ti)O_3$ -based (PZT-based) composites that contained fine silver particles were fabricated and the authors proposed novel-type processing strategy in ferroelectric materials that satisfies the recent demand for multifunctional and high-performance ferroelectric materials. This paper addresses the effect of silver particle addition on the Curie temperature of a PZT-based composite. The Curie temperature anomaly is discussed in terms of the substitution of the silver ion and the two types of internal (residual) stress—(i) internal thermal stress, or internal stress induced by thermal expansion mismatch between the matrix and dispersoids, and (ii) transformation-induced internal stress.

II. Experimental Procedure

The fabrication of PZT-based composites that contained fine silver particles was performed by using the conventional powder metallurgical method. Starting materials were commercially available PZT (PE510, Fuji Titanium Co., Tokyo, Japan) and silver(I) oxide (Ag_2O) (Wako Pure Chemical Co., Osaka, Japan) powders. Characteristics of the starting materials and processing details have been described in our previous paper.¹⁰ PZT- Ag_2O powder mixtures were fired at 900° or 1000°C for 1 h in an atmosphere that was controlled by PbO -rich powder (lead titanate, $PbZrO_3$). Heating and cooling rates were 300°C/h and 1000°C/h, respectively. Typical specimens were 10 mm in diameter and 1 mm thick. Sintered specimens were ground using 400- and 800-grit resin-bond diamond wheels and further polished using 9, 3, and 0.5 μm diamond pastes, in sequence, for microstructure observation.

Bulk density was measured via the Archimedes method in water. The grain size of composites was determined from micrographs taken using scanning electron microscopy (SEM), using a linear-intercept method. The average linear intercept (L) was measured, and then $L(\pi/2)$ was considered to be the average grain size, G . To evaluate the dielectric properties, silver paste was printed on both sides of a disk-shaped specimen and then fired at 600°C for 10 min. Dielectric properties such as capacitance and loss tangent, together with their temperature dependence, were measured using an impedance analyzer (Model HP 4194A, Hewlett-Packard, Tokyo, Japan) by changing the specimen temperature from room temperature to 450°C at 1 kHz. All the measurements were conducted in an air atmosphere. The microstructure was observed by using SEM.

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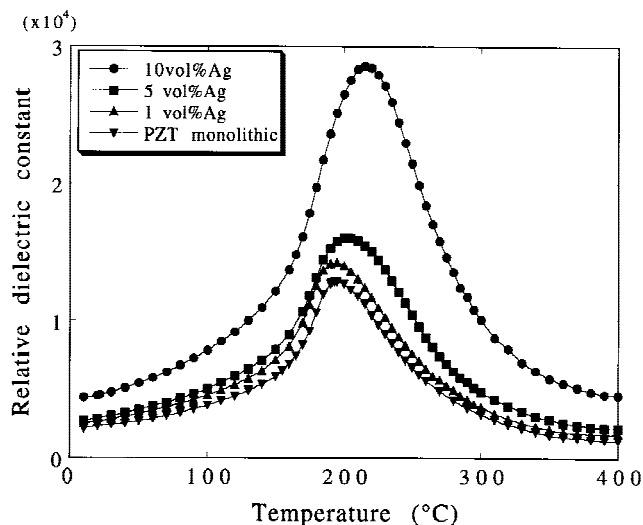


Fig. 1. Effect of silver addition on the temperature dependence of the dielectric constant for monolithic PZT and PZT/silver composites sintered at 1000°C for 1 h.

III. Results and Discussion

The temperature dependence of the relative dielectric constant for monolithic PZT and PZT/silver composites sintered at 1000°C for 1 h is shown in Fig. 1. Fully densified samples could be obtained when sintered at temperatures >900°C, except for monolithic PZT that had no silver particles.¹⁰ Relative densities were 89.4% and 98.2% for monolithic PZT sintered at 900° and 1000°C, respectively. All the samples exhibited similar temperature dependencies of the dielectric constant at the temperature that corresponded to the ferroelectric-to-paraelectric phase transformation (~200°C). PZT/silver composites exhibited the higher relative dielectric constant at room temperature, as well as at the Curie temperature. In this study, electrically conductive silver particles have been homogeneously dispersed in the PZT matrix,¹⁰ so that the relative dielectric constant is expected to increase according to Maxwell's equation.¹¹

Another feature that is observed in Fig. 1 is that the Curie temperature shifts to a higher temperature when the silver content increases. The Curie temperatures for monolithic PZT and PZT/silver composites sintered at 1000°C for 1 h are summarized in Fig. 2, as a function of silver content. The Curie temperature linearly increases as the silver content increases.

Some papers have described the change in the Curie temperature for barium titanate (BaTiO₃) and lead lanthanum zir-

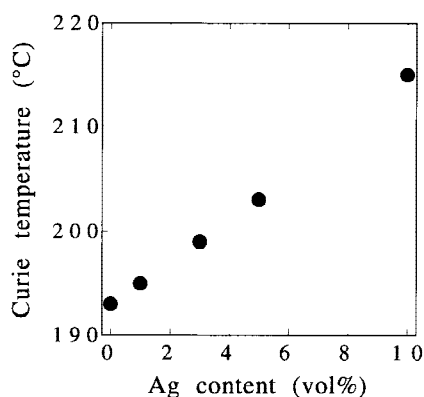


Fig. 2. Curie temperature change for PZT/silver composites sintered at 1000°C as a function of the silver content.

conate titanate ((Pb,La)(Zr,Ti)O₃) and its related ceramics with changes in the silver addition.^{12–14} According to the previous reports, the Curie temperature decreases as the silver content increases. This phenomenon has been discussed in connection with the silver substitution in the A-site of the perovskite crystal structure. However, the result in this study is the opposite of these reports. As Fig. 2 shows, the Curie temperature is increased by the incorporation of silver particles. Therefore, the shift in the Curie temperature that is observed in the PZT/silver composite could not be explained by the silver substitution into the perovskite crystal structure of PZT.

The Curie temperature can be considered to be influenced by the internal thermal stresses that are caused by the thermal expansion mismatch between the matrix and the silver. Because the thermal expansion coefficients of the PZT matrix and silver phases are $13 \times 10^{-6}/^{\circ}\text{C}$ and $28 \times 10^{-6}/^{\circ}\text{C}$, respectively, considerable amounts of residual stresses are introduced into the matrix grains and silver particles during the cooling process from the sintering temperature. The real stress at any point of the matrix can be determined as the uniform average stress, σ_{mr} , plus the locally fluctuating stress that is developed by the nearby particles, σ_{fr} .¹⁵ In the present case, σ_{mr} is compressive in the matrix, and, according to Taya *et al.*,¹⁶ σ_{mr} can be approximately estimated to be 125 MPa for a 10 vol% silver composite, assuming the temperature difference, Young's modulus, and Poisson's ratio of silver to be 1000°C, 75 GPa, and 0.380, respectively; the measured Young's modulus and Poisson's ratio via the ultrasonic pulse method were 78 GPa and 0.371, respectively, for PZT. Using the expression derived by Selsing,¹⁷ σ_{fr} can be expressed as

$$\sigma_{fr} = \frac{\Delta\alpha\Delta T}{\frac{1 + \nu_m}{2E_m} + \frac{1 - 2\nu_d}{E_d}}$$

where $\Delta\alpha$ is the difference in thermal expansion coefficients between the matrix and the dispersoid, and ΔT is the cooling range; E and ν are the Young's modulus and Poisson's ratio, respectively (the subscripts "m" and "d" denote the matrix and dispersoid, respectively). The locally fluctuating stress σ_{fr} can be a function of the distance from the nearby particle; σ_{fr} is estimated to be ~1249 MPa in tension in the radial direction and ~624 MPa in compression in the tangential direction at the matrix/particle interface.

Thus, there are two effects that the internal thermal stresses have on the Curie temperature behavior of PZT/silver composites. The first effect is a broadening of the phase-transformation behavior. In the PZT/silver composites, the silver particles are mainly dispersed at junctions of three or more grains. If the *c*-axis of a PZT matrix grain is parallel to the radial direction of the surrounding silver particles, the grain transforms at higher temperature (i.e., the Curie temperature increases because the *c*-axis has been expanded by a residual tensile stress). On the other hand, if the *c*-axis is perpendicular to the radial direction of silver, the Curie temperature shifts to a lower temperature. Consequently, the Curie temperatures of the individual grains have a wider distribution than those with no secondary dispersoid, depending on how the *c*-direction is related to the orientation to the silver particles.

The other effect is that the Curie temperature of perovskite ceramics is reduced. Although the residual thermal stress field is very anisotropic, the average stress in the matrix is compressive, as stated. This compressive stress causes the Curie temperature to decrease. Thus, the residual thermal stress effect cannot explain why the Curie temperature increases as the silver content increases.

When polycrystalline ferroelectrics are cooled through their transformation temperature, an internal stress develops because the individual grain is clamped by its neighboring grains. However, such transformation-induced internal stresses can be relaxed by such events as the formation of 90° twinning in the crystallites, the presence of a pore or flaw, or the presence of a

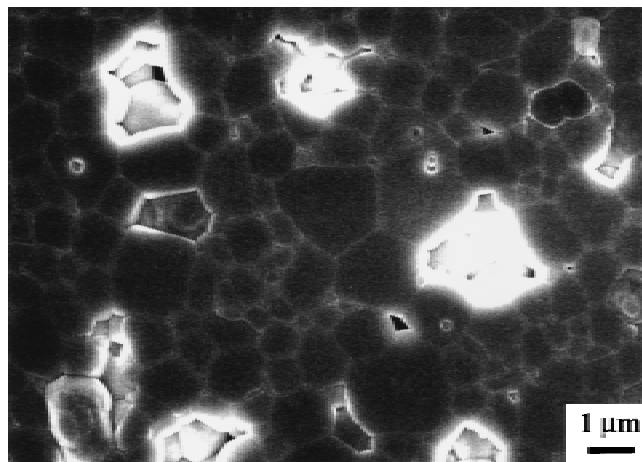


Fig. 3. SEM micrograph of a polished and thermally etched PZT/10 vol% silver composite sintered at 1000°C for 1 h.

grain-boundary phase. In particular, the internal stress of ferroelectric ceramics is significantly reduced as the porosity increases.^{18,19} If the internal stress decreases via the above-mentioned mechanisms, the Curie temperature shifts to a higher temperature and approaches the value of a single crystal. Thus, the Curie temperature of polycrystalline ferroelectrics is strongly dependent on their microstructure, such as the grain-size and grain-boundary condition and density. The Curie temperature of some perovskite-type ceramics has been reported to be a microstructure-sensitive property.^{8,9}

Figure 3 shows an SEM micrograph of a polished and thermally etched PZT/10 vol% silver composite sintered at 1000°C. The pores observed in Fig. 3 are sites where silver particles have been pulled out by polishing or evaporated during etching. Silver particles were primarily located at grain boundaries or triple-grain junctions when sintering was performed at temperatures <900°C.²⁰ On the other hand, silver particles >2 μm in size are surrounded by four or more matrix grains, as shown in Fig. 3. According to our previous study,¹⁰ the particle size of silver increased as the sintering temperature increased. In this study, the average particle size of silver was 1.4 μm for the 10 vol% silver composites sintered at 900°C, whereas it increased up to 2.8 μm when the composite was sintered at 1000°C. This abrupt increase is very likely caused by the coalescence of silver particles, because of the high sintering temperature (above the melting point of silver, 953°C). Silver particles that were initially located at grain boundaries or triple-grain junctions coalesce with the grain growth of the PZT matrix when the sintering temperature is increased up to 1000°C.

The transformation-induced internal stress can be reduced by 90° domain (twin) formation, as noted previously. The internal stress near the grain boundary is known to be substantially greater than that in the grain because of the interaction between the grain boundary and the 90° domain.^{18,19} In other words, the grain boundary limits the internal stress relief by forming the 90° domains, and the internal stress is concentrated at the grain boundary.²¹ In the PZT/silver composite, the ductile character of silver particles at the grain boundaries, therefore, would accommodate the strain that is induced by paraelectric-to-ferroelectric transformation, because the mechanical constraint at the PZT/silver interface is less than that at the PZT grain boundary, and it is expected that the concentration of the internal stress would be significantly relieved.

Our separate study²⁰ revealed that the three-point bending strength of monolithic PZT was higher at temperatures above the Curie temperature than at room temperature. However, there is no strength difference for the PZT/10 vol% silver composite between room temperature and temperatures above the

Curie temperature. This observation means that the internal stress was relieved by silver addition, because the observed strength difference must be attributed to the existence of the internal stress.¹⁸

In this regard, the Curie temperature anomaly that has been observed in PZT/silver composites might be associated with the relaxation of internal stress by silver particles dispersed in the PZT matrix. It might be speculated that intergranular silver particles can effectively absorb local strains produced by transformation and relax internal stress of the PZT matrix grains, in a manner similar to that of pores. As a consequence, the Curie temperature increases as the silver content increases, as shown in Fig. 2.

IV. Summary

The Curie temperatures of PZT/silver composites shift to higher temperatures as the silver content increases. This shift in the Curie temperature has been discussed in terms of silver substitution, internal thermal stress due to the thermal expansion mismatch between the matrix and silver, and the relaxation of transformation-induced internal stress.

Some silver may substitute for the lead ion during the sintering process and is capable of modifying the Curie temperature. However, the increase in the Curie temperature cannot be solved by the silver substitution, because it produces oxygen vacancies, which are known to decrease the Curie temperature.

Compressive internal stress, which is caused by the larger thermal expansion of silver than the matrix, remains in the matrix. In this regard, the Curie temperature should decrease in the PZT/silver composite. Nevertheless, the Curie temperature result contradicts the prediction from consideration of the internal thermal stress.

The relaxation of transformation-induced internal stresses by intergranular silver particles is the most-likely mechanism responsible for the increase in the Curie temperature that is observed in PZT/silver composites. It is suggested that silver particles at the grain boundary can reduce the interaction between the grain boundary and 90° domains, and, as a result, the transformation-induced internal stress of the matrix grain that is near the silver particle can be effectively relieved by the ductile behavior of the silver particle.

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