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Process Window of $BaTiO_3$–Ni Ferroelectric–Ferromagnetic Composites

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Experimental study and thermodynamic analysis are conducted to identify a process window for the preparation of $BaTiO_3$–Ni ferroelectric–ferromagnetic composites. A tiny amount of Ni solutes ($<$0.5 mol%) can play a key role in the preparation of the composites. The Ni solute acts as an acceptor that enhances the reduction resistance of $BaTiO_3$. Owing to the presence of Ni acceptors, dense $BaTiO_3$–Ni composites can be prepared by sintering above 1330°C in an atmosphere of 1 Pa oxygen partial pressure.

I. Introduction

Barium titanate ($BaTiO_3$) is a ferroelectric material with a perovskite structure. It can form solid solution with many ions.[1] The properties of $BaTiO_3$ can thus be modified through the solution with various ions. $BaTiO_3$-based materials therefore exhibit versatile properties and many useful applications. Nickel is a ferromagnetic material with a reasonable oxidation resistance at room temperature. The $BaTiO_3$–Ni system thus offers an interesting combination of ferroelectric and ferromagnetic characteristics.

The most important application for the $BaTiO_3$–Ni system is the base-metal-electrode multilayered ceramic capacitors (BME–MLCC). In order to manufacture BME–MLCC, the $BaTiO_3$-based dielectrics are first co-fired with Ni inner electrodes at a temperature above 1200°C in a highly reducing atmosphere $\left(P_{O_2} = 10^{-5} \sim 10^{-7}\,\text{Pa}\right)$ and then annealed at about 1000°C in an atmosphere of higher oxygen partial pressure $\left(P_{O_2} = 10^{-2} \sim 10^{-4}\,\text{Pa}\right)$ to re-oxidize the dielectrics.[2] In these dielectrics, many oxides, such as CaO, MnO, and Y_2O_3 are doped as acceptors to enhance the reduction resistance of $BaTiO_3$. However, several studies have indicated that Ni may also dissolve into $BaTiO_3$[3–8] with a solubility value ranging from 0 to 8000 ppm.[9,10] This scatter in solubility is likely to result from the difference in the composition of the $BaTiO_3$-based dielectrics and from the techniques used to determine the solubility. With a continuous trend of decreasing dielectric thickness, the interaction between $BaTiO_3$ and Ni may alter the performance of MLCC. It is therefore essential to investigate the effects of interaction between $BaTiO_3$ and Ni on the performance of MLCC.

Furthermore, Pecharroman *et al.*[11] suggested that the dielectric constant of $BaTiO_3$ could be significantly increased by adding 3 μM metallic Ni particles. A dielectric constant as high as 80 000 was measured by Pecharroman and colleagues when an amount approaching the percolation limit (31 vol%) of Ni was added to $BaTiO_3$. Another study suggested that the toughness of $BaTiO_3$ could be enhanced significantly through the addition of 5 vol% nano-sized Ni particles.[9] These existing studies indicate that the $BaTiO_3$–Ni composite is a promising material system. However, after conducting preliminary thermodynamic and sintering studies, the preparation of composites containing pure $BaTiO_3$ and pure Ni turned out to be a very challenging task. The main objective of the present study is therefore to identify a process window for the preparation of $BaTiO_3$–Ni composites. The following targets are expected to be achieved when adopting the processing conditions given by the process window:

(1) High in density: the density of the $BaTiO_3$–Ni composites should be high enough ($>$90%) for possible practical applications.

(2) Ferroelectric characteristics: the $BaTiO_3$–Ni composites should possess ferroelectric characteristics that give rise to high dielectric constant and insulation resistance.

(3) Ferromagnetic characteristics: the Ni in the $BaTiO_3$–Ni composites should remain in its metallic state after sintering. The ferromagnetic characteristics of metallic Ni can therefore be maintained.

The present study will demonstrate that by manipulating the oxygen partial pressure, a small amount of Ni ions from the metallic Ni can be dissolved into $BaTiO_3$. The presence of Ni^{2+} acceptors is sufficient to enhance the reduction resistance of $BaTiO_3$. A process window exists for the preparation of the $BaTiO_3$–Ni composites without the addition of other dopants.

II. Experimental Procedure

The barium titanate ($BaTiO_3$) powder (NEB, Ferro Electronic Material System, Penn Yan, NY) and various amounts of nickel nitrate (ACROS Organics Co., Morris Plains, NJ) were tumble-milled together in ethyl alcohol for 4 h. The Ba/Ti ratio of the $BaTiO_3$ powder was 1.000 ± 0.002 as reported by the manufacturer. The grinding media used were ZrO_2 balls. The slurry of the powder mix was dried using a rotary evaporator. The dried lumps were then crushed and passed through a #200 plastic sieve. The powder was then calcined in air at 500°C for 2 h to remove NO_x. The powder was uniaxially pressed into sample disks at 25 MPa.The disks were 10 mm in diameter and about 3 mm in thickness. The disks were then fired at 800°C for 2 h in a 95% N_2/5% H_2 atmosphere in order to reduce the NiO into Ni. The morphology of the particles of the disks was investigated using transmission electron microscopy (TEM, 100 KV, JEOL Co., Tokyo, Japan). The amount of Ni in the powder mixture was determined by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, 3000DV, Perkin Elmer, Optima, Wellesley, MA).

Sintering was performed at 1330°, 1370°, or 1400°C for 2 h in one of the following atmospheres: air, N_2, or an N_2/H_2 mixture in a tube furnace. The heating and cooling rates were set at 3°C/min. A zirconia oxygen sensor, placed 1–2 mm above the specimens, was used to monitor the oxygen partial pressure during sintering. The oxygen partial pressure in the sintering atmosphere was measured at 2×10^4 Pa in air, 1–10 Pa in N_2, and 10^{-2}–10^{-5} Pa in an N_2/H_2 mixture (depending on the mixing ratio) at 1330°–1400°C. Phase identification was performed by X-ray diffractometry (XRD, PW 1830, Philips Co., Eindhoven, the Netherlands) at a scanning rate of 0.05° 2θ/s. A very slow

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scanning rate (0.002° 2θ/s) was also adopted to determine the lattice constant ratio, *c*/*a*, using the (002) and (200) reflections.

The dielectric permittivity was measured by an LCR meter (HP4284A, Agilent Co., Palo Alto, CA) at 1 kHz. The Curie temperature was determined from the resulting permittivity–temperature curve. The electrical resistivity was measured using the two-probe method at 50 V and room temperature (617 Programmable electrometer, Keithley Co., Cleveland, OH). The magnetization curve for the specimen was obtained by a SQUID magnetometer (MPMS7, Quantum Design Co., San Diego, CA).

III. Results

(1) Interactions Between BaTiO$_3$ and Ni

The XRD analyses indicate that only BaTiO$_3$ and NiO are present in the powder mixture after calcining at 500°C in air, and BaTiO$_3$ and Ni in the sample compacts after reducing at 800°C in the 95% N$_2$/5% H$_2$ atmosphere. Figure 1 shows the morphology of the BaTiO$_3$–Ni powder mixture after reduction. The sizes of the BaTiO$_3$ and Ni particles are around 500 and 60–70 nm, respectively. Figure 2 shows the XRD patterns of the pure BaTiO$_3$ and BaTiO$_3$–Ni specimens after sintering at 1330°C for 2 h. Pure BaTiO$_3$ remains in tetragonal form after sintering in all the atmospheres used in the present study. The Ni particles in the BaTiO$_3$–Ni powder compacts are fully oxidized when the sintering is carried out in air. Both Ni and NiO are found in the BaTiO$_3$–Ni specimens sintered in the atmospheres with oxygen partial pressures of 1–10 Pa and 10^{-2}–10^{-3} Pa. No NiO can be found in the BaTiO$_3$–Ni specimens when the oxygen partial pressure of the sintering atmosphere is reduced to 10^{-4}–10^{-5} Pa.

By slowing down the scanning rate for the XRD analysis, the tetragonality (*c*/*a* ratio) of BaTiO$_3$ can be calculated from the (200) and (002) peaks as shown in Fig. 3. The *c*/*a* ratio remains the same with increasing Ni when the sintering is carried out in the highly reducing atmosphere, i.e. $\left(P_{\mathrm{O}_2} = 10^{-4} 10^{-5}\,\mathrm{Pa}\right)$. This indicates that there is no Ni dissolved into the BaTiO$_3$ lattice. However, the *c*/*a* ratio is no longer a constant as the oxygen partial pressure in the sintering atmosphere is increased above 10^{-3} Pa. The *c*/*a* ratio decreases from 1.010 to a minimum plateau as the Ni content is higher than 0.05–0.075 vol% (i.e., 0.38–0.52 mol%), suggesting that an amount between 0.05 and 0.075 vol% of Ni is capable of dissolving into the BaTiO$_3$ lattice after sintering. The value of the minimum plateau for the *c*/*a* ratio decreases with increasing oxygen partial pressure of the sintering atmosphere, suggesting that the solubility of Ni in BaTiO$_3$ increases with increasing oxygen partial pressure. The measured Curie temperatures of the composites sintered in air also confirm that the solubility of Ni in BaTiO$_3$ is between 0.05 and 0.075 vol%.

Figure 4 shows the relative densities of the BaTiO$_3$–Ni specimens sintered at various temperatures and in various atmospheres. The densities for most specimens are higher than 90%. Generally speaking, the addition of Ni particles reduces the sintering activity of BaTiO$_3$. Exaggerated grain growth can be found in the BaTiO$_3$–0.075% Ni and BaTiO$_3$–0.1% Ni specimens after sintering in air $\left(P_{\mathrm{O}_2} = 2 \times 10^4\,\mathrm{Pa}\right)$. The densities of these two specimens are therefore lower than 90%.

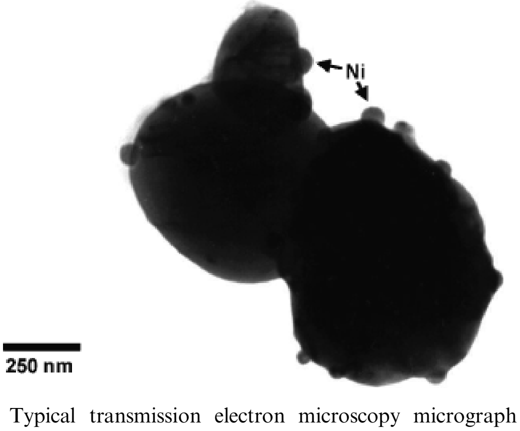

Fig. 1. Typical transmission electron microscopy micrograph of a BaTiO$_3$–5% Ni powder mixture after reduction in a 95% N$_2$/5% H$_2$ atmosphere at 800°C for 2 h $\left(P_{\mathrm{O}_2} = 10^{-7}\,\mathrm{Pa}\right)$.

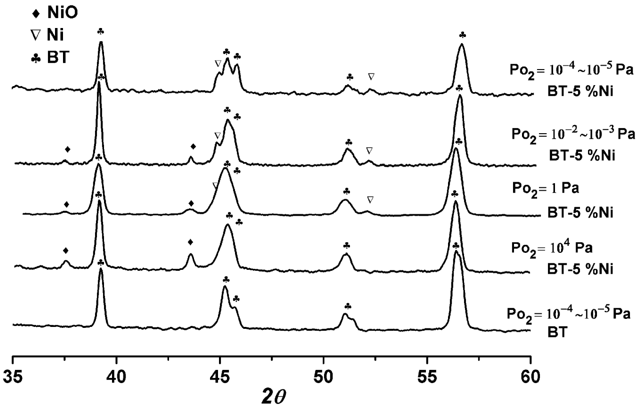

Fig. 2. XRD patterns of BaTiO$_3$ (BT) and BaTiO$_3$–5% Ni (BT–5% Ni) specimens after sintering at 1330°C in various atmospheres.

(2) Electrical and Magnetic Properties

Figure 5 shows the electrical resistivities of the BaTiO$_3$–Ni specimens sintered at 1330°–1400°C in various atmospheres. All the specimens, including pure BaTiO$_3$, were pre-fired in a highly reducing atmosphere $\left(P_{\mathrm{O}_2} = 10^{-7}\,\mathrm{Pa}\right)$ to reduce NiO to Ni first. However, such a treatment also reduces the electrical resistivity. For the BaTiO$_3$–Ni specimens sintered in air, their electrical resistivities are more or less the same, all higher than $10^{10}\ \Omega \cdot \mathrm{m}$. However, the electrical resistivity of pure BaTiO$_3$ remains low after sintering in an atmosphere of $P_{\mathrm{O}_2} = 1$ Pa. Nevertheless, the electrical resistivity increases to above $10^{10}\ \Omega \cdot \mathrm{m}$ when Ni is added. The situation is similar for the specimens sintered in $P_{\mathrm{O}_2} = 10^{-2} \sim 10^{-3}$ Pa, except that a slightly higher Ni content is needed to increase the electrical resistivity to above $10^{10}\ \Omega \cdot \mathrm{m}$. For the specimens sintered in $P_{\mathrm{O}_2} = 10^{-4} \sim 10^{-5}$ Pa, the electrical resistivity reduces to below $10^{7}\ \Omega \cdot \mathrm{m}$.

Figure 6 shows the magnetization curves for the BaTiO$_3$ and BaTiO$_3$–Ni composites. The specimens shown in the figure were sintered at 1330°C in $P_{\mathrm{O}_2} = 1$ Pa. Both Ni and NiO are present in the BaTiO$_3$–Ni composites. Table I shows the magnetic characteristics of the BaTiO$_3$–Ni composites with the addition of 1 and 5 vol% Ni; the composites exhibit paramagnetic features.

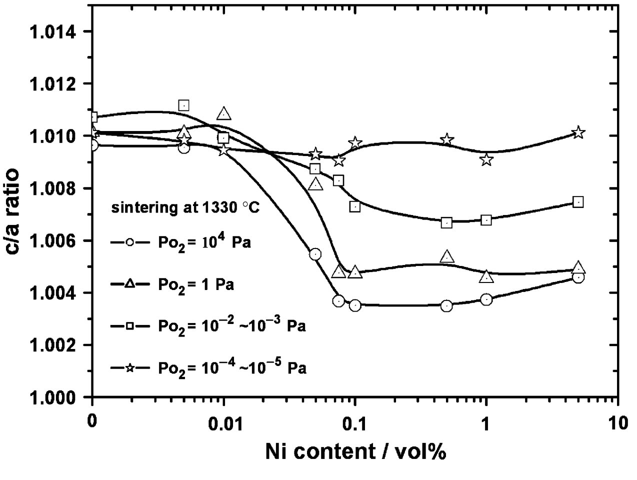

Fig. 3. Tetragonality (*c*/*a* ratio) of BaTiO$_3$ crystal as a function of Ni content. BaTiO$_3$–Ni specimens are sintered at 1330°C for 2 h at various oxygen partial pressures.

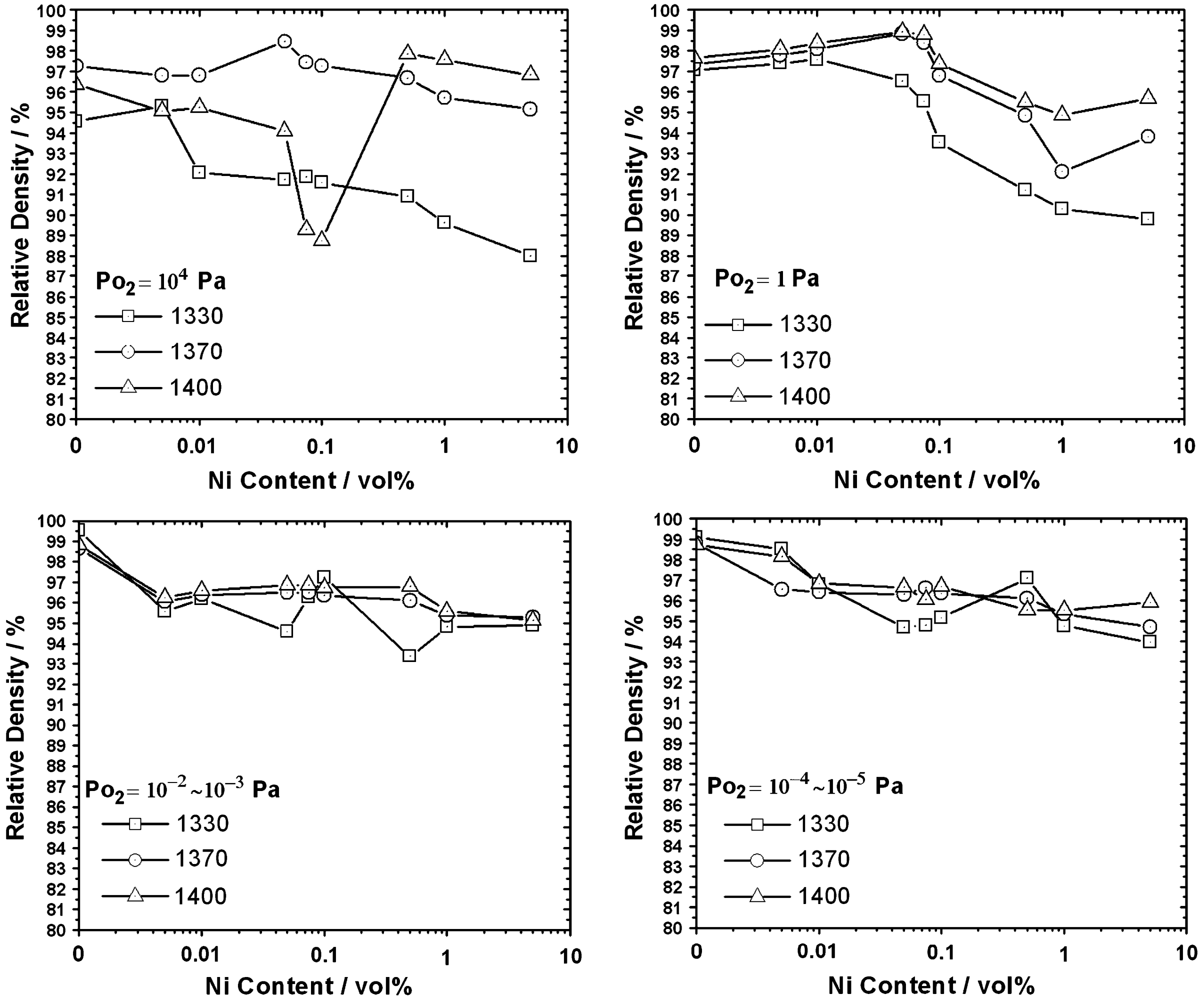

Fig. 4. Relative density of $BaTiO_3$–Ni specimens after sintering at various temperatures at various oxygen partial pressures.

IV. Discussion

(1) *Thermodynamic Analysis*

Although metallic nickel is relatively resistant to oxidation under an ambient condition, it can readily be oxidized in an environment of high oxygen partial pressure at an elevated temperature as shown in the following reaction:

$$Ni + \tfrac{1}{2}O_2 \rightarrow NiO \tag{1}$$

The standard free energy for the above reaction is[12]

$$\Delta G = 235600 - 86T\ (\mathrm{J/mol}) \tag{2}$$

In order to avoid the oxidation of nickel, the sintering of $BaTiO_3$–Ni has to be carried out in an atmosphere of low oxygen partial pressure. Figure 7 shows the equilibrium oxygen partial pressure of the Ni/NiO reaction as a function of temperature. The oxygen partial pressure in the sintering atmosphere has to be lower than the values shown on the Ni/NiO line to avoid the oxidation reaction.

Although barium titanate is an oxide with high electrical resistivity, it becomes an *n*-type semiconductor after firing in a highly reducing atmosphere as demonstrated in the following reaction[10,13–15]:

$$O_O^x \leftrightarrow V_O^{\bullet\bullet} + 2e' + \tfrac{1}{2}O_2 \tag{3}$$

According to the above equation, the amount of free electrons increases with decreasing oxygen partial pressure, and consequently the electrical resistance is reduced. The decrease of electrical resistance could jeopardize the ferroelectric properties of $BaTiO_3$.

The reaction constant, K_n, of Reaction (3) can be expressed as

$$K_n = \frac{[V_O^{\bullet\bullet}]n^2 P_{O_2}^{1/2}}{[O_O^x]} \tag{4}$$

The increase of oxygen partial pressure could promote the filling of oxygen vacancies and the formation of electron holes (*p*-type conductor) as[10,13–15]

$$\tfrac{1}{2}O_2 + V_o^{\bullet\bullet} \leftrightarrow O_o^x + 2h^\bullet \tag{5}$$

The reaction constant, K_p, of reaction (5) can be expressed as

$$K_p = \frac{[O_O^x]p^2}{P_{O_2}^{1/2}[V_O^{\bullet\bullet}]} \tag{6}$$

When the concentrations of electrons and electron holes are the same, the electrical conductivity is the lowest, and the critical oxygen partial pressure, $P_{O_2}^*$, can be estimated by the following relationship derived from Eqs. (4) and (6):

$$P_{O_2}^* = \frac{K_n}{K_p}\frac{[O_O^x]^2}{[V_O^{\bullet\bullet}]^2} \tag{7}$$

The oxygen partial pressure in the sintering atmosphere should be set close to this critical value to avoid a decrease in the electrical resistance. Although the effect of oxygen partial

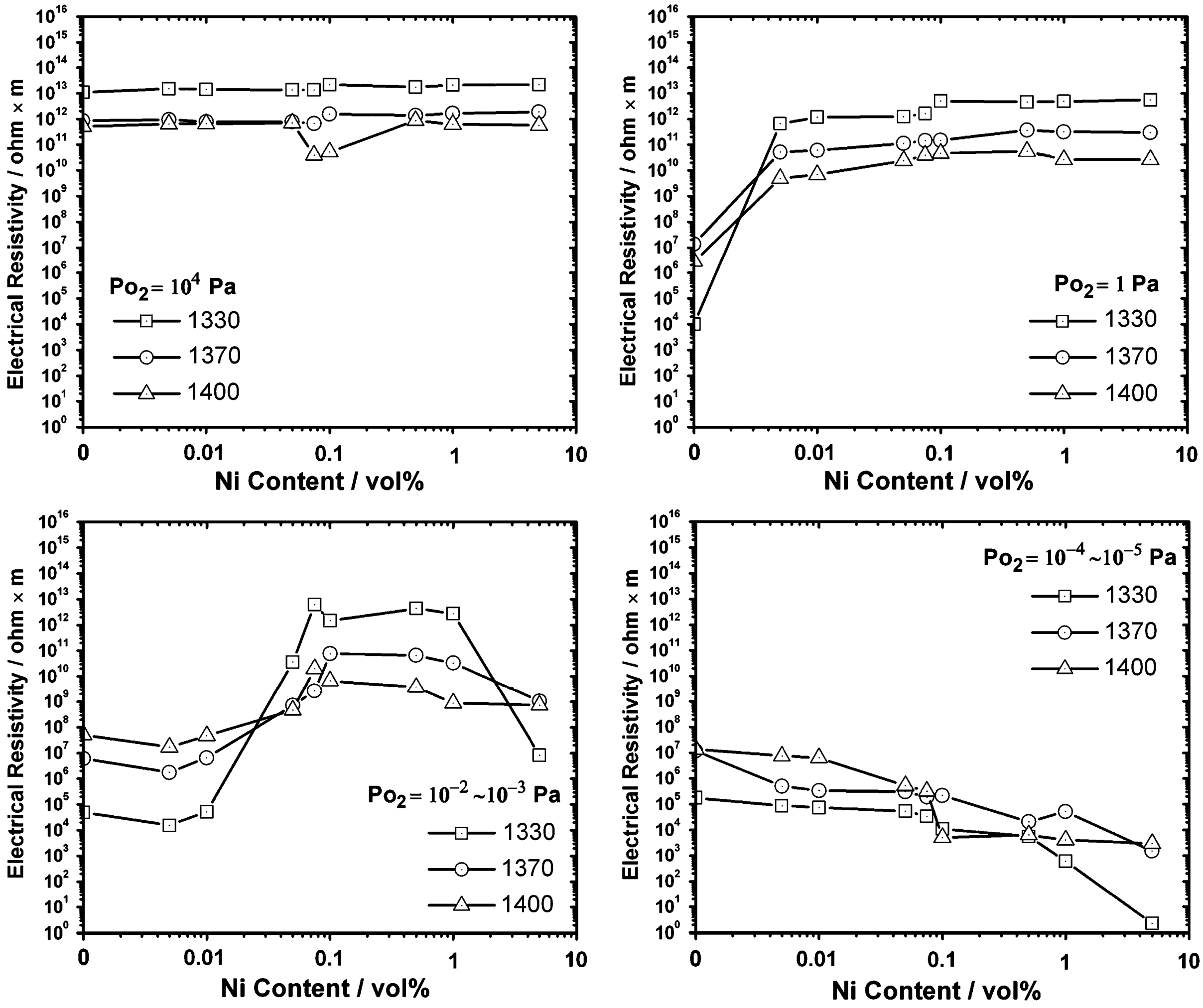

Fig. 5. Electrical resistivity of $BaTiO_3$–Ni specimens after sintering at various temperatures at various oxygen partial pressures.

pressure on the electrical conductivity of $BaTiO_3$ is well documented,[10,13–15] the existing data show conflicting results. For example, the reported values for K_n from two research groups differ by an order of magnitude.[13,15] Moreover, the value of K_p has not yet been reported. Impurities within the raw materials such as Na^+ or K^+ may substitute Ba^{2+}, and Al^{3+} or Fe^{3+} may substitute Ti^{4+}.[13] The charges of these impurities are lower than the charges of their substituting ions. These impurities are therefore mainly acceptors to $BaTiO_3$. The total concentration of impurities is usually unknown. Without knowing the concentration of oxygen vacancies and the values of K_n and K_p, it is not possible to calculate the value of the critical oxygen partial pressure using Eq. (7).

Alternatively, it is possible to determine the value of $P^*_{O_2}$ by adopting the experimental approach described in the present study. Figure 7 shows the electrical resistivity of pure $BaTiO_3$ as a function of oxygen partial pressure in a sintering atmosphere and at a sintering temperature. The data shown in Fig. 7 are marked with different symbols to represent different electrical resistivities. As the oxygen partial pressure in the sintering atmosphere is above 1 Pa, the electrical resistivity of $BaTiO_3$ is higher than 10^{10} $\Omega \cdot m$, which is the minimum requirement for dielectric applications. However, the electrical resistivity decreases to $<10^{10}$ $\Omega \cdot m$ as the oxygen partial pressure in the sintering atmosphere decreases to below 10^{-2} Pa. The electrical resistivity of $BaTiO_3$ declines to a much lower value, $<10^4$ $\Omega \cdot m$, when it is sintered in a highly reducing environment ($<10^{-4}$ Pa). Figure 7 indicates that the value of $P^*_{O_2}$ falls within the range between 10^{-2} and 1 Pa. However, as the $BaTiO_3$ specimen is reduced first in a highly reducing atmosphere (95% N_2/5% H_2,

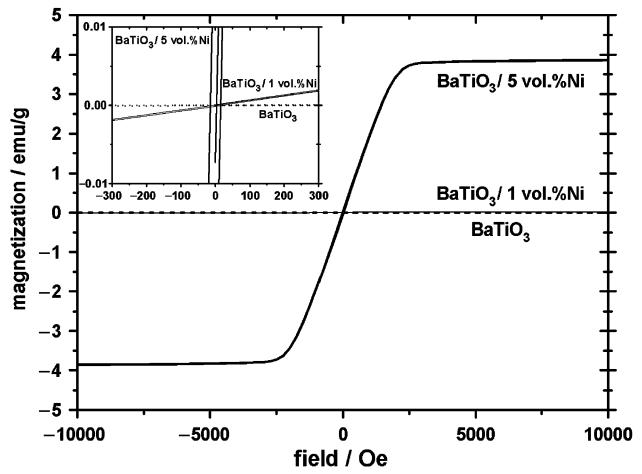

Fig. 6. Magnetization curves for $BaTiO_3$, $BaTiO_3$–1% Ni, and $BaTiO_3$–5% Ni specimens at room temperature.

Table I. Magnetic Characteristics of $BaTiO_3$–Ni Composites After Sintering at 1330°C in $P_{O_2} = 1$ Pa

Ni content (vol%)	0	1†	5†
Saturation magnetization (emu/g)	0.002	0.015	3.9
Coercivity (Oe)	131	14	14

†Part of the Ni is oxidized to NiO during sintering.

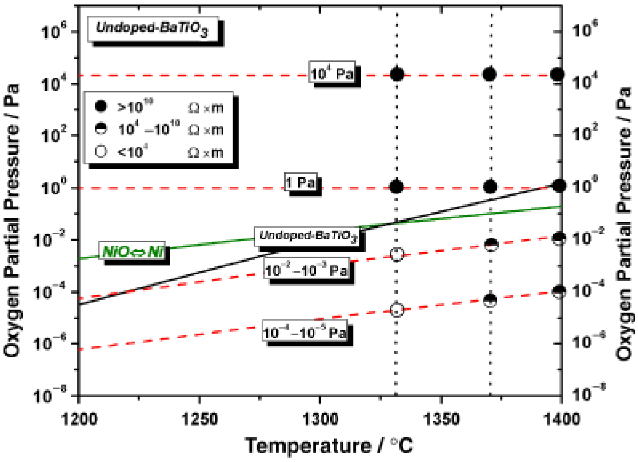

Fig. 7. Equilibrium oxygen partial pressure for the Ni/NiO reaction and critical oxygen partial pressure, $P^*_{O_2}$, to produce insulating BaTiO$_3$.

$P_{O_2} = 10^{-7}$ Pa) at 800°C and then sintered at 1330°–1400°C in $P_{O_2} = 1$ Pa, the electrical resistivity of the specimen is also lower than 10^{10} $\Omega \cdot$m. This suggests that the $P^*_{O_2}$ is relatively closer to 1 Pa within the sintering temperature range investigated. Thus, 1 Pa is assumed to be the value of $P^*_{O_2}$ in Eq. (7) at a sintering temperature of 1400°C. As the activation energy of K_n in Eqs. (4) and (7) has been reported to be −520 kJ/mol,[15] assuming that K_p and $[V_O^{\bullet\bullet}]$ are less sensitive to temperature change, the $P^*_{O_2}$ at other temperatures can thus be calculated. The $P^*_{O_2}$ as a function of temperature is shown as a black solid line in Fig. 7.

From Fig. 7, the $P^*_{O_2}$ line intersects the Ni/NiO line at 1330°C, suggesting that the BaTiO$_3$–Ni composites can only be obtained by sintering at a temperature below 1330°C in order to avoid a decrease in the electrical resistivity and maintain the metallic state of Ni. However, for the BaTiO$_3$ powder used in the present study, the density of pure BaTiO$_3$ is lower than 90% as the sintering temperature is below 1330°C. The above theoretical analysis implies that the process window for the preparation of dense BaTiO$_3$–Ni composites does not exist.

(2) *Solubility of Ni in BaTiO$_3$*

The XRD analysis demonstrates that there are no chemical reactions between BaTiO$_3$ and Ni. However, a small amount of Ni may dissolve into BaTiO$_3$ during co-firing at elevated temperatures. The solubility of a dopant in BaTiO$_3$ depends not only on the charge but also on the radius of the dopant.[1] Although the charge of the Ni^{2+} ion is the same as that of the Ba^{2+} ion, the radius of the Ni^{2+} ion (0.069 nm) is close to that of the Ti^{4+} ion (0.0605 nm).[16] Several techniques have been used to determine the solubility of various dopants in BaTiO$_3$.[1,3–8,17–19] The most popular ones involve the measurement of the Curie temperature and lattice parameters. The values of Curie temperature are affected by many factors.[13] As the two peaks BaTiO$_3$ (002) and (200) are very close to each other, a calibration on the c/a ratio is not needed to ensure its accuracy. Therefore, only the data for the lattice parameter measurement are present. Figure 3 suggests that the solubility of Ni in BaTiO$_3$ depends strongly on the oxygen partial pressure in the sintering atmosphere. As $P_{O_2} > 10^{-3}$ Pa, the solubility of Ni in BaTiO$_3$ increases with increasing oxygen partial pressure. As P_{O_2} is as low as 10^{-5} Pa, the solution of Ni into BaTiO$_3$ is suppressed.

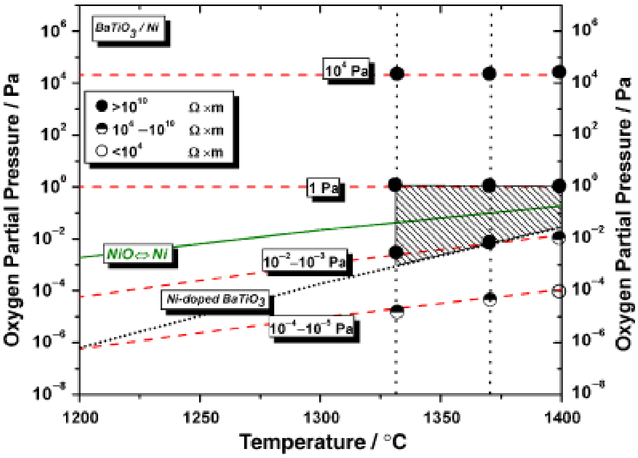

Fig. 8. Process window (shadow area) for BaTiO$_3$–0.075 vol% Ni composites. Within this window, the relative density of BaTiO$_3$–Ni composites is higher than 90% and electrical resistivity is higher than 10^{10} $\Omega \cdot$m. Equilibrium oxygen partial pressure for the Ni/NiO reaction and critical oxygen partial pressure, $P^*_{O_2}$, to produce insulating BaTiO$_3$–Ni composites are also shown.

By assuming that Ti^{4+} is replaced by Ni^{2+} and Ni^{2+} acts as an acceptor to BaTiO$_3$, the solution of Ni into BaTiO$_3$ can be expressed by the following reaction:

$$\mathrm{Ni} \xrightarrow{\mathrm{BaTiO_3}} \mathrm{Ni}''_{\mathrm{Ti}} + V_{\mathrm{O}}^{\bullet\bullet} \tag{8}$$

Reactions (3) and (8) are competing for the available oxygen vacancies. The addition of Ni^{2+} acceptors increases the $[V_O^{\bullet\bullet}]$(Reaction (8)) and consequently reduces the concentration of electrons (Reaction (3)). The reduction of oxygen partial pressure increases the concentration of oxygen vacancies and also suppresses Reaction (8). The decrease of oxygen partial pressure thus decreases the solubility of the acceptor, which has also been suggested by Bheemineni *et al.*[14] As the solubility of Ni in BaTiO$_3$ decreases with decreasing oxygen partial pressure, it is confirmed that the Ni^{2+} solutes act as acceptors to BaTiO$_3$.

As the introduction of acceptors can induce the formation of oxygen vacancies and suppress the formation of electrons in BaTiO$_3$, the insulation resistance of BaTiO$_3$ is increased as Ni is added. Equation (8) also suggests that the concentration of nickel dopant is the same as that of oxygen vacancy as:

$$[\mathrm{Ni}''_{\mathrm{Ti}}] = [V_{\mathrm{O}}^{\bullet\bullet}] \tag{9}$$

Therefore, Eq. (6) can be transformed into the following equation as:

$$P^*_{O_2} = \frac{K_n}{K_p} \frac{[\mathrm{O}_\mathrm{O}^x]^2}{[\mathrm{Ni}''_{\mathrm{Ti}}]^2} \tag{10}$$

The above equation indicates that the critical oxygen partial pressure, $P^*_{O_2}$, decreases with increasing acceptor concentration.

(3) *Process Window of BaTiO$_3$–Ni Composites*

The electrical properties such as dielectric constant, dissipation factor, and electrical resistivity have strong connections among them. As the insulation resistivity is high, the corresponding dissipation factor is usually small.[20] In the present study, the electrical resistivity is used as the key index for the evaluation of the ferroelectric–ferromagnetic composites. Figure 8 shows the electrical resistivity of the BaTiO$_3$–Ni specimen containing 0.075 vol% Ni as a function of oxygen partial pressure and sintering temperature. The Ni content is close to the solubility of Ni in BaTiO$_3$. The density of all the specimens shown in Fig. 8 is higher than 90%.

The data in Fig. 8 are grouped into three parts according to their electrical resistivity: $>10^{10}$, 10^4–10^{10}, and $<10^4$ $\Omega \cdot$m. For the BaTiO$_3$–Ni specimens sintered at 1330° and 1350°C in $P_{O_2} > 10^{-3}$ Pa, their electrical resistivities are higher than 10^{10} $\Omega \cdot$m. The electrical resistivity of the BaTiO$_3$–Ni specimen sintered at 1400°C in $P_{O_2} > 10^{-3}$ Pa is slightly lower than 10^{10} $\Omega \cdot$m, but still $>10^9$ $\Omega \cdot$m. This indicates that the line of critical oxygen pressure $P^*_{O_2}$ versus temperature is close to 10^{-2}–10^{-3} Pa. By forcing the reduction resistance line of BaTiO$_3$–Ni to pass 1370°C, the process window (the shadow region in Fig. 8) for the $BaTiO_3$–Ni composites can thus be defined. It is evident that the process window of the $BaTiO_3$–Ni composite is significantly larger than that of pure $BaTiO_3$. As the $P^*_{O_2}$ is lowered by two orders of magnitude, the solubility of Ni in $BaTiO_3$ is around 10 times the original impurity content in the starting $BaTiO_3$ powder (see Eq. 10).

Within the process window, the density of most $BaTiO_3$–Ni composites is higher than 90% and the electrical resistivity is higher than 10^{10} $\Omega \cdot m$. The composites prepared according to the conditions indicated by the window are thus ferroelectric materials. The saturated magnetization (M_s) of $BaTiO_3$–5% Ni reaches a value of 3.9 emu/g. The maximum M_s value of pure Ni is 55 emu/g.[21] This indicates that the paramagnetic performance of the Ni particles surrounded by the $BaTiO_3$ matrix can be fully utilized. The M_s of $BaTiO_3$–1% Ni is rather low. This may due to the oxidation of the Ni particles after sintering in $P_{O_2} = 1$ Pa.

Metallic Ni is maintained in the $BaTiO_3$–Ni composites sintered in an atmosphere of $P_{O_2} = 1$ Pa. Such an oxygen partial pressure is higher than the equilibrium oxygen partial pressure for the Ni–NiO reaction, suggesting that the fine Ni particles are well protected by the surrounding $BaTiO_3$ matrix. It may also suggest that a period of 2 h at a temperature of 1330°–1400°C is not long enough to oxidize the Ni particles fully. However, NiO is also found in the composites sintered at an oxygen partial pressure of 10^{-2}–10^{-3} Pa, which is below the equilibrium oxygen partial pressure of the Ni–NiO reaction. The fine Ni particles in the $BaTiO_3$–Ni green compacts were fully reduced before sintering. One may argue that the Ni particles are oxidized under an ambient condition before sintering. However, we would like to propose an alternative possibility. Chan *et al.*[13] and Nowtney and Rekas[15] have both proposed the values for the reaction constants, K_n, of Reaction (3). By using their reaction constants, the Gibbs free energy of Reaction (3) at 1330°C is estimated as -520 and -360 kJ/mol, respectively. The Gibbs free energy of the Ni/NiO reaction (Eq. (1)) at 1330°C is -98 kJ/mol. As $BaTiO_3$ and Ni are mixed together and co-fired at elevated temperatures in a low oxygen partial pressure atmosphere, the reduction of $BaTiO_3$, (Eq. (3)), prevails. However, part of the Ni remains after sintering.

The addition of Ni acceptors enhances the reduction resistance of $BaTiO_3$. The reduction line for $BaTiO_3$ is thus pushed downward in terms of oxygen partial pressure due to the addition of Ni solutes. The process window is large enough to prepare dense $BaTiO_3$–Ni ferroelectric–ferromagnetic composites.

V. Conclusions

In the present study, the process window for the $BaTiO_3$–Ni composites is established. The solution of Ni into $BaTiO_3$ plays a key role in the preparation of the ferroelectric–ferromagnetic composites. The presence of Ni solutes enlarges the process window. In order to dissolve Ni into $BaTiO_3$, the oxygen partial pressure in the sintering atmosphere should be higher than 10^{-3} Pa. By using the processing conditions given by the process window, dense $BaTiO_3$–Ni composites ($>90\%$ relative density) with ferroelectric and ferromagnetic characteristics can be prepared.

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