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A study of $BaTiO_3$–$BaPbO_3$ ceramic composites

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Abstract. The ceramic composites prepared from donor-doped ceramic $BaTiO_3$ and the conducting ceramic $BaPbO_3$ are studied in the present paper. The XRD result shows that the composites consist of the $BaTiO_3$ phase and the $BaPbO_3$ phase. An abrupt decrease in the curve of resistivity versus $BaPbO_3$ content was observed; this was explained by the three-dimensional percolation model for the two-phase $BaTiO_3$–$BaPbO_3$ composite, and the percolation volume threshold ϕ_c obtained was near 0.14. Beyond the percolation threshold, the electrical transport properties of the composites are similar to those of $BaPbO_3$ ceramics, The positive temperature coefficient effect found in donor-doped $BaTiO_3$ disappears above a $BaPbO_3$ volume fraction of about 0.04.

1. Introduction

It has been reported that some perovskite-type structure oxide ceramics show a high electrical conductivity in a wide temperature range [1]. For example, the resistivity of barium metaplumbate ($BaPbO_3$) ceramics is about $5.0 \times 10^{-4}\ \Omega$ cm at room temperature [2].

On the other hand, rich and varied physical phenomena exist in perovskite-type $BaTiO_3$ ceramics. For example, donor-doped $BaTiO_3$ semiconducting ceramics exhibit an insulator-to-semiconductor phase transition and an anomalous increase in the resistivity near the Curie temperature T_C, known as the positive temperature coefficient (PTC) effect [3].

In recent years, composite materials such as organic–inorganic composites and metal–inorganic composites have received considerable attention. However, composites of two kinds of electrical ceramics (such as ferroelectric semiconductive ceramics and conducting ceramics) have rarely been investigated [4].

The present paper is mainly concerned with the phase structure and electrical properties of the ceramic composites of the $BaTiO_3$–$BaPbO_3$ system.

2. Experiments

The samples were prepared by the mixed-oxide method. The starting materials were $BaTiO_3$ powder (containing 1 mol% SiO_2, 0.14 mol% Nb_2O_5 and 1 mol% excess of TiO_2) according to the stoichiometry of the semiconducting ceramics, and $BaPbO_3$ powder (with 6 at.% excess of Pb), which were calcined at 1150 °C for 1 h and at 900 °C for 6 h, respectively. The nominal composition is $(1-\phi)$ $BaTiO_3$–ϕ $BaPbO_3$, where the volume fractions ϕ of

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$BaPbO_3$ are 0.04, 0.08, 0.12, 0.16, 0.24, 0.34, 0.43 and 1, respectively. The calcinations of $BaTiO_3$ powder and $BaPbO_3$ powder were weighed according to the compositions and then wet mixed in an agate ball mill. After drying, the powders were pressed into discs. Finally, the samples were sintered at 1200–1330 °C for 10–30 min and annealed at 500 °C for 4 h in air. The normal heating rate is about 400 °C h^{-1} and the fast heating rate is about 600-800 °C h^{-1} at high temperatures. The ceramic densities of samples for $0.04 \leqslant \phi \leqslant 0.43$ are in the range from 5.4 to 6.0 g cm^{-3}, and the density of the $BaPbO_3$ ceramics (for $\phi = 1$) is 7.46 g cm^{-3}. The relative densities of all samples are greater than 90% at different heating rates.

The resistivity was measured by the four-probe method in the temperature range from 10 K to 800 K. X-ray powder diffraction was carried out at room temperature using Cu Kα radiation to determine the crystalline structure.

3. Results and discussion

Two phases were observed in the $BaTiO_3$–$BaPbO_3$ ceramic composite. Their typical x-ray diffraction patterns are shown in figure 1. When the $BaPbO_3$ content ϕ is 0.04, only the tetragonal $BaTiO_3$ phase was observed by XRD. When the $BaPbO_3$ content increases, e.g. $\phi = 0.12$ the diffraction peaks of the $BaPbO_3$ phase appear; its diffraction intensity also increased with increasing $BaPbO_3$ content. When $\phi = 0.24$, the two-phase patterns of $BaTiO_3$ and $BaPbO_3$ are predominant. No obvious deviation in unit-cell size was observed. This indicates that the ceramic composite mainly consists of the $BaTiO_3$ phase and the $BaPbO_3$ phase.

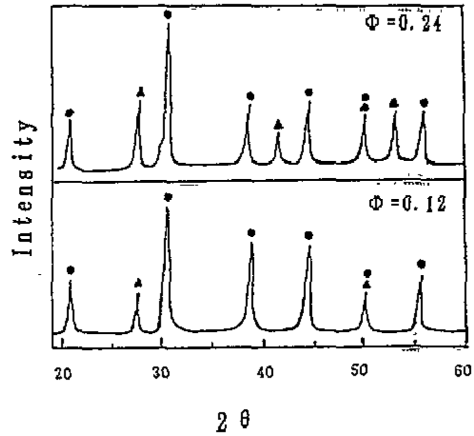

Figure 1. Typical XRD pattern of the $(1 - \phi)$ $BaTiO_3$–$\phi BaPbO_3$ system for $\phi = 0.12$ and 0.24: ●, $BaTiO_3$ phase; ▲, $BaPbO_3$ phase.

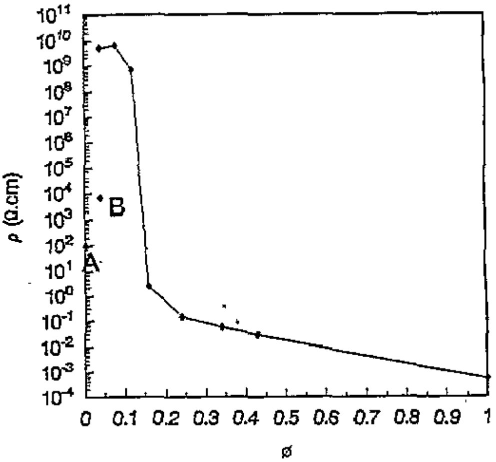

Figure 2. Composition dependence of resistivity of the ceramic composites of the $(1 - \phi)$ $BaTiO_3$–$\phi BaPbO_3$ system: ——, samples heated at normal heating rates (400 °C h^{-1}); data point A, donor-doped semiconducting $BaTiO_3$ ceramic of single phase; data point B, sample of ceramic composite for $\phi = 0.04$ heated at fast heating rates (600–800 °C h^{-1}).

Figure 2 shows the electrical resistivity ρ curve as a function of $BaPbO_3$ content ϕ in the $BaTiO_3$–$BaPbO_3$ ceramic composites. It can be divided into three composition ranges.

(1) For $0 < \phi \leqslant 0.12$, the resistivity of the ceramic composites is high (about $10^9\ \Omega$ cm), and it is independent of the $BaPbO_3$ content at the normal heating rate (about 400 °C h^{-1}), which is represented by the solid line. The high resistivity of the composites for $\phi \leqslant 0.12$ arose because of the resistivity of the $BaTiO_3$ phase. It is well known that the heating rates, dopants and second phases have great influence on the semiconducting property of donor-doped $BaTiO_3$ ceramics. Here, the low resistivity of the donor-doped $BaTiO_3$ phase was not obtained owing to the influence of the $BaPbO_3$ phase, especially when the samples were sintered at the normal heating rate.

(2) For $0.12 \leqslant \phi \leqslant 0.24$, the resistivity decreased abruptly from 10^9 to $1\ \Omega$ cm, and it is sensitive to the variation in the $BaPbO_3$ content. In general, the resistivity of donor-doped semiconducting $BaTiO_3$ ceramics is not lower than $10\ \Omega$ cm. The resistivity of the composites for $0.12 \leqslant \phi \leqslant 0.24$ which decreased to $1\ \Omega$ cm was attributed to the increasing proportion of the $BaPbO_3$ phase.

(3) For $0.24 \leqslant \phi \leqslant 1$, the resistivity of the composites is in the range from 1 to $10^{-4}\ \Omega$ cm, which is relatively low.

The abrupt decrease in resistivity of the ceramic composite can be explained by the three-dimensional percolation model [4,5]. The percolation threshold ϕ is defined as the volume fraction at which conducting paths begin to form. That is, for $\phi < \phi_c$, the volume fraction of the $BaPbO_3$ phase is very low, the segregation of limited clusters predominates and the material cannot conduct; at $\phi = \phi_c$, an infinite continuous $BaPbO_3$ grain cluster begins to form conducting pathways and the material conducts, resulting in a low resistivity. Finally, in the range $0.24 \leqslant \phi \leqslant 1$, the resistivity decreases to a saturation value, wherein the resistivity is relatively insensitive to the volume fraction of the conducting phase owing to extensive interparticle contacts. Here the resistivity of the composite is expected to approach that of the conducting $BaPbO_3$ phase.

According to the three-dimensional scaling theory, in the vicinity of the percolation threshold in a random distributed two-phase system, the conductivity of the composite materials can be expressed by the percolation equation [5]

$$\sigma \sim (\phi - \phi_c)^t$$

where $t = \frac{8}{5}$ when $\phi > \phi_c$, and ϕ_c is the percolation threshold. The conductivity $\sigma^{5/8}$ versus ϕ curve is plotted in figure 3 using the resistivity ρ versus ϕ curve (solid line) in figure 2. The straight line in figure 3 extrapolated to $\sigma = 0$ gives the intercept $\phi_C \simeq 0.14$. This critical volume fraction ϕ_c fits the theoretical value of the three-dimensional percolation threshold of 0.16 ± 0.02 [5] well. From the above discussion, it is concluded that the conductivity of the materials follows the percolation behaviour in the two-phase ceramic system consisting of $BaTiO_3$ and $BaPbO_3$. This result further shows that the $BaPbO_3$ phase and the $BaTiO_3$ phase are independent and randomly distributed in the ceramic composite.

The data for the resistivity versus temperature for the $(1-\phi)\,BaTiO_3$–$\phi BaPbO_3$ ceramic composites with $\phi = 0.16$, 0.24, 0.34, 0.43 and 1 are shown in figure 4. No temperature dependence of resistivity is obvious, as is typical of $BaPbO_3$ ceramics. In this composition range, the predominant conductive network in the ceramic composite is the $BaPbO_3$ phase. The PTC effect found in donor-doped $BaTiO_3$ was not observed for $\phi \geqslant 0.12$.

For low $BaPbO_3$ contents ($0 < \phi \leqslant 0.12$), the resistivity of the composites (about $10^9\ \Omega$ cm) at the normal heating rate (about 400 °C h^{-1}) is greater than that of

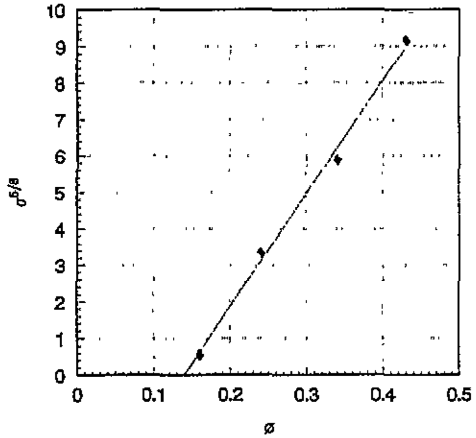

Figure 3. Resistivity $\sigma^{5/8}$ versus $BaPbO_3$ volume fraction ϕ in the $(1-\phi)$ $BaTiO_3$–ϕ $BaPbO_3$ system.

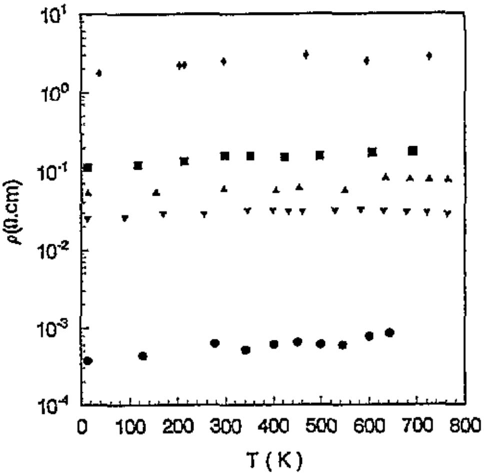

Figure 4. Temperature dependence of resistivity in the temperature range from 10 to 800 K for the $(1-\phi)$ $BaTiO_3$–ϕ $BaPbO_3$ system for various ϕ: ♦, $\phi = 0.16$; ■, $\phi = 0.24$; ▲, $\phi = 0.34$; ▼, $\phi = 0.43$; ●, $\phi = 1$.

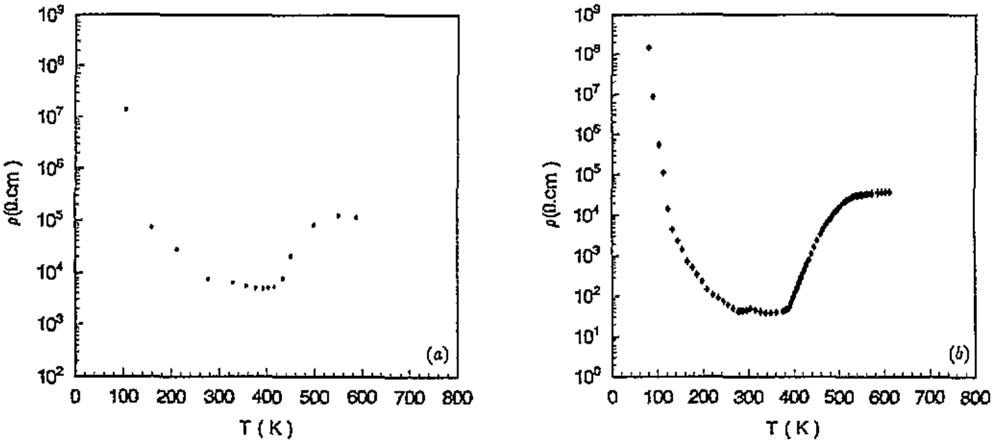

Figure 5. Temperature dependences of resistivity in the temperature range from 10 to 300 K for (*a*) $\phi = 0.04$ in the $(1-\phi)$ $BaTiO_3$–$\phi BaPbO_3$ system and (*b*) donor-doped semiconducting $BaTiO_3$ of single phase (i.e. $\phi = 0$).

semiconducting $BaTiO_3$ PTC ceramics of single phase (about 10^2 Ω cm at room temperature as represented by data point A for $\phi = 0$ in figure 2). This is because of the influence of the $BaPbO_3$ phase and the sintering process. When the manufacturing process of the ceramics is modified, the resistivity of the composite ceramics can be decreased to a low value only for very low $BaPbO_3$ contents. For instance, the resistivity of the sample for $\phi = 0.04$ is about 6×10^3 Ω cm at room temperature (data point B) by sintering at fast heating rates (600–800 °C h^{-1}) in the high-temperature range from 1150 °C to the sintering temperature and a short sintering time (10 min) at the sintering temperature. The temperature dependence of resistivity for this sample shows a PTC effect at about 420 K, as illustrated in figure 5(*a*), similar to that of semiconducting $BaTiO_3$ PTC ceramics. The temperature dependence of the resistivity of the single-phase $BaTiO_3$ semiconducting ceramics is shown in figure 5(*b*).

4. Conclusion

Two-phase ceramic $BaTiO_3$–$BaPbO_3$ composites were successfully prepared. The conduction behaviour of this ceramic composite is fitted to the three-dimensional percolation model and the percolation threshold ϕ_c is about 0.14. When the volume fraction of the $BaPbO_3$ phase is higher than the percolation threshold, the electrical properties of the composites are those of the $BaPbO_3$ phase and, when the volume fraction of the $BaPbO_3$ phase is 0.04, the ceramic composites show the PTC property of the $BaTiO_3$ semiconducting ceramics obtained by an appropriate manufacturing process.

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