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ABSTRACT

A class of ceramic composite prepared with two kinds of oxide ceramics of ferroelectric $BaTiO_3$ and superconducting $YBa_2Cu_3O_{6+\delta}$ was reported, and the phase structure and electrical transport properties of the samples were investigated. The results show that the main phases varied in different composition regions. For low nominal $YBa_2Cu_3O_{6+\delta}$ content, the conductive characteristics of the two-phase ($BaTiO_3$ and $YBa_3Ti_2O_{8.5}$) composite follow the three-dimensional percolation model; while for high nominal $YBa_2Cu_3O_{6+\delta}$ contents, superconductivity was observed.

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I. INTRODUCTION

Perovskite-type oxides have received considerable attention since the discovery of high Tc superconducting oxide ceramics in the field of solid state physics. There exist rich and varied physical phenomena in these oxide ceramics, whose properties are closely related to the composition and structure of the materials[1,2]. For instance, high temperature superconductivity in $YBa_2Cu_3O_{6+\delta}$ ceramics is obtained by drawing electrons from the anti-ferromagnetic base; and the ferroelectric $BaTiO_3$ and $SrTiO_3$ by means of doping undergo insulator-to-semiconductor-to-conductor (superconductor) phase transitions[3,4]. Hence detailed investigation on the physical properties in the materials is meaningful.

Moreover, various composite materials[5,6] with excellent performance superior to single material have been prepared with the development of materials science. Recently, the progress in research and application of the composite materials is amazing, such as metal/ ceramic composites, polymer/ ceramic composites and so on. However, the composite material consisting of two different kinds of functional ceramics is rarely reported. The present paper is mainly concerned with the phase structure and electrical transport properties of the polycrystalline composite materials of ferroelectric $BaTiO_3$ and superconducting $YBa_2Cu_3O_{6+\delta}$ system.

II. EXPERIMENTS

The samples of the ceramic composite were prepared with sintered $BaTiO_3$ and sintered $YBa_2Cu_3O_{6+\delta}$ powders by means of solid state reaction. The nominal composition is $(1-\phi)$ $BaTiO_3$ – ϕ

$YBa_2Cu_3O_{6+\delta}$, where the volume fraction ϕ of $YBa_2Cu_3O_{6+\delta}$ is 0, 0.05, 0.10, 0.16, 0.18, 0.20 ,0.30, 0.40, 0.45, 0.55, 0.60, 0.65, 0.70, 0.80, and 0.90, respectively. The powders were weighed, mixed, dried and pressed into pellets. The pellets were then sintered at their best centring temperatures, respectively, to obtain high quality specimens.

The resistivity was measured by four-probe method in a temperature range of 10K-300K. X-ray powder diffraction using Cu Kα radiation was carried out on samples at room temperature to determine the crystallographic structure.

III. RESULTS AND DISCUSSION

1. Phase structure

Various phases were observed in different nominal composition regions for the ceramic composite prepared from ferroelectric $BaTiO_3$ ceramics and superconducting $YBa_2Cu_3O_{6+\delta}$ ceramics. Their typical X-ray diffraction patterns of the samples are shown in Fig.1 a), b), c). The composition can be divided into three parts according to the XRD results.

(1). In the low nominal content range of $YBa_2Cu_3O_{6+\delta}$ for $0 \le \phi \le 0.45$ (denoted as region I), it is observed that the predominant phases are $BaTiO_3$ and $YBa_3Ti_2O_{8.5}$ and there also existed a little $BaCuO_2$ phase and CuO phase. In this composition region, the sintering temperature of the samples was 1180°C, which is much higher than that of $YBa_2Cu_3O_{6+\delta}$ phase (980°C). It is probable that $YBa_2Cu_3O_{6+\delta}$ phase was integrated under this sintering condition and further reacted with Ti element to form a new phase of $YBa_3Ti_2O_{8.5}$, which was reported recently. The phase $YBa_3Ti_2O_{8.5}$ can be written in a term of $(Y_{0.5}Ba_{1.5})TiO_{4+\delta}$, representing the Ba-sites of Ba_2TiO_4 phase partly substituted by Y element.

(2). In the higher content of $YBa_2Cu_3O_{6+\delta}$ for $0.60 \le \phi < 1$ (denoted as region III), $YBa_2Cu_3O_{6+\delta}$ phase was formed, for the sintering temperature in these compositions was decreased to 1050°C x 1hr, close to the sintering temperature for $YBa_2Cu_3O_{6+\delta}$ superconductor. The predominant phases become $YBa_2Cu_3O_{6+\delta}$ and $YBa_3Ti_2O_{8.5}$, and a little $BaCuO_2$ and CuO phases still exist. But $BaTiO_3$ phase was not observed in this composition range.

(3). Between regions I and III for $0.45 < \phi < 0.60$, there existed a transition region denoted as region II. In this region, the results of XRD show that the main phase was $YBa_3Ti_2O_{8.5}$ and there exist a little $YBa_2Cu_3O_{6+\delta}$, $BaTiO_3$, $BaCuO_2$ and CuO phases.

2. Conduction of the functional ceramic composite

The resistivity of the samples is closely related to the nominal content ϕ, as well as the phase structure, as shown in Fig.2. At ϕ=0, the resistivity of the $BaTiO_3$ is about 3×10^7 Ωcm. For $\phi \le 0.40$, an abrupt decrease in resistivity in the vicinity of a certain content ϕ, instead of linear decrease, was observed, and then the resistivity decreases almost linearly for $\phi \ge 0.45$. These electrical transport behaviour arose from the variation of the phase structure of materials and the conductivity of each phase, which is discussed as follows.

(1) The percolation conductivity in region I ($0 < \phi \le 0.45$)

It is clear that the main phases in region I are $BaTiO_3$ and $YBa_3Ti_2O_{8.5}$ and the proportion of $YBa_3Ti_2O_{8.5}$ phase increases while the proportion of $BaTiO_3$ phase decreases with the increasing content ϕ according to the above XRD results. The grains of $YBa_3Ti_2O_{8.5}$ phase were randomly incorporated into the $BaTiO_3$ matrix from the viewpoint of microstructure. The whole resistivity is dependent upon the volume proportion and the resistivity of the two phases in the composite materials consisting of $BaTiO_3$ and $YBa_3Ti_2O_{8.5}$ phases.

Fig. 2 shows the composition dependence of resistivity. For $0 \le \phi \le 0.10$, the high resistivity of the composite is indicative of the high resistive phase $BaTiO_3$. For ϕ in a narrow range from 0.16 to 0.20, the resistivity decreases abruptly from 10^9 Ω.cm to 10^4 Ω•cm The percolation threshold ϕ is defined as the volume fraction at which conducting paths begin to form. Namely, for $\phi < \phi_c$, the segregation of limited clusters predominates and the material cannot conduct for the volume fraction of $YBa_3Ti_2O_{8.5}$ phase is much low ; at $\phi = \phi_c$, an infinite continuous $YBa_3Ti_2O_{8.5}$ grain cluster begins to form conducting pathways and the material conduct, resulting in low resistivity. Finally in the range of $0.20 \le \phi \le 0.45$, the resistivity decreases to a saturation value, wherein the resistivity is relatively insensitive to the volume fraction of the conducting phase due to extensive inter particle contacts. Here the resistivity of the composite is expected to approach that of the conducting $YBa_3Ti_2O_{8.5}$ phase.

From the above discussion, it is drawn that the conductivity of the materials follow the percolation behaviour in a two-phase system consisting of $BaTiO_3$ and $YBa_3Ti_2O_{8.5}$ and it is prospected that the resistivity of $YBa_3Ti_2O_{8.5}$ phase is lower than that of $BaTiO_3$ phase.

In a system composed of a high conductive phase and a low conductive phase of random distribution, according to the three-dimensional percolation theory, in the vicinity of the percolation threshold, there exists a characteristic length of transition and it can be expressed as[7,8]:

$$\xi \sim |\phi-\phi_c|^{-v} \quad (1)$$

where ϕ is the percentage of high conductive phase and ϕ_c is the percolation threshold. The physical properties of the composite materials are related to the characteristic length ξ. For instance the conductivity of the composite materials can be expressed by the percolation equation as follows:

$$\sigma(\phi>\phi_c) \sim \xi^{-t/v} \sim |\phi-\phi_c|^{t} \quad (2)$$

$$\sigma(\phi<\phi_c) \sim \xi^{s/v} \sim |\phi_c-\phi|^{-s} \quad (3)$$

where critical exponents t and s are constants, which are dependent upon the dimension of the percolation system. It is reported that t equals to 1.6 and s equals to 1 in the three-dimensional materials. So the percolation threshold can be obtained by the following method. For t=1.6, equation (2) can be expressed as the follows:

$$\sigma(\phi>\phi_c) \sim |\phi-\phi_c|^{1.6} = |\phi-\phi_c|^{8/5} \quad (4)$$

Namely, $\sigma(\phi>\phi_c)^{5/8} \sim |\phi-\phi_c|$ (5)

The $\sigma^{5/8}$ versus ϕ curve was plotted in Fig.3 according to the lgρ versus x curve in Fig.2. The straight line in Fig.3 extrapolated σ=0 intercepts $\phi_c \approx 0.17$. This critical volume fraction is in well agreement with the theoretical value of three-dimensional percolation threshold of 0.16±0.02[4]. This result further shows that $YBa_3Ti_2O_{8.5}$ phase and $BaTiO_3$ phase are randomly distributed in the ceramic composite.

(2). Conductivity in region II ($0.45 < \phi < 0.60$)

In this region, the results of XRD show that the main phase is $YBa_3Ti_2O_{8.5}$ and there is a little $YBa_2Cu_3O_{6.8}$, $BaTiO_3$, $BaCuO_2$ and CuO phases. The electrical properties of the samples mainly indicated the characteristics of doped $YBa_3Ti_2O_{8.5}$ phase. The resistivity of samples in region II is ranged from 10^2 to 10^3 Ω•cm, and it is nearly independent of temperature as shown in Fig.2 and Fig.4.

The electrical transport behavior of the single $YBa_3Ti_2O_{8.5}$ phase, as well as the doped $YBa_3Ti_2O_{8.5}$ phase needs further study.

(3). Superconductivity in region III ($0.60 \leq \phi < 1$)

In region III, the X-ray diffraction results indicate that the ceramic composite mainly consists of $YBa_2Cu_3O_{6+\delta}$ phase and $YBa_3Ti_2O_{8.5}$ phase for $0.65 \leq \phi < 1$. The percolation behaviour similar to region I should have occurred, for the resistivity of $YBa_2Cu_3O_{6+\delta}$ phase is much lower than that of $Ba_3Ti_2O_{8.5}$ phase. In fact, the resistivity of the composites decreases almost linearly with increasing nominal content ϕ, as shown in Fig.2. The measured temperature dependence of resistivity of the composites in a temperature range from 10K to 300K for ϕ=0.60, 0.65, 0.80, and 0.90 is showed in Fig.4 and Fig.5. The resistivity of the composite material is about 10^1 $\Omega \cdot cm$ for ϕ=0.6 and it shows semiconductive behavior in low temperatures. As the $YBa_2Cu_3O_{6+\delta}$ nominal content increases further, for ϕ=0.8 and 0.9, weak negative temperature characteristic occurs initially, then at 60-70K the resistivity drastically decreases, and the superconducting transition occurs at much lower temperatures.

The previous results on the single phase $YBa_2Cu_3O_{6+\delta}$ indicated that the low temperature dependence of resistivity of $YBa_2Cu_3O_{6+\delta}$ system undergoes a transition from the semiconducting behavior to the metal conducting behavior and the corresponding resistivity at the room temperature decreases, as the oxygen content δ increases[3].

The above experimental results of the composites in region III are related to the proportion of $YBa_2Cu_3O_{6+\delta}$ phase as well as its oxygen content δ. In the low $By_2Cu_3O_{6+\delta}$ nominal content, the oxygen content δ in $YBa_2Cu_3O_{6+\delta}$ phase is much low, and the resistivity of the composite which depends upon that of $YBa_2Cu_3O_{6+\delta}$ phase is high, and the semiconducting behavior of resistivity in low temperatures similar to that of $YBa_2Cu_3O_{6+\delta}$ with low oxygen content is observed. As the proportion of $YBa_2Cu_3O_{6+\delta}$ phase increases, and the oxygen content δ of $YBa_2Cu_3O_{6+\delta}$ phase increases, the resistivity of the $YBa_2Cu_3O_{6+\delta}$ phase decreases and hence the resistivity of the whole ceramic composite decreases. This is in agreement with the results of the $YBa_2Cu_3O_{6+\delta}$ superconducting ceramics[3]. The percolation behavior similar to region I does not occur, although the resistivity of $YBa_2Cu_3O_{6+\delta}$ phase is much lower than that of $Yba_3Ti_2O_{8.5}$ phase, which is due to the oxygen content as well as the resistivity of the $YBa_2Cu_3O_{6+\delta}$ phase varied in the whole composition range of region III. These results indicated that the oxygen content δ in the $YBa_2Cu_3O_{6+\delta}$ superconducting ceramics is easily lost in preparing these ceramic composites, which needs to smooth over in the next experimental work.

In addition, it is observed that the effect of magnetic flux pinning and the critical current density is enhanced because of the existence of the little second phases in the ceramic composite. It is also found that there probably exists negative resistance effect. These interesting phenomena in the ceramic composite need further study.

The present work shows that mechanical mixture of two kinds of functional ceramics is obtained by means of proper manufacturing process; and there exist rich and varied physical phenomena in this new class of material, whose development will promote the development of new functional materials, new properties and new applications.

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FIGURE CAPTIONS

Figure 1 Typical X-ray Diffraction Pattern of the samples

a) ϕ =0.30, 0.40, 0.45, 0.50

b) ϕ =0.55

c) ϕ =0.60, 0.65, 0.70

Figure 2 Composition dependence of resistivity of the samples

Figure 3 Curve of $\sigma^{5/8}$ versus ϕ

Figure 4 Temperature dependence of resistivity in a temperature range from 10K to 300K for ϕ=0.55, 0.60

Figure 5 Temperature dependence of resistivity in a temperature range from 10K to 300K for ϕ=0.90, 0.80, 0.65

Curve 1: ϕ=0.90; Curve 2: ϕ=0.80; Curve 3: ϕ=0.65

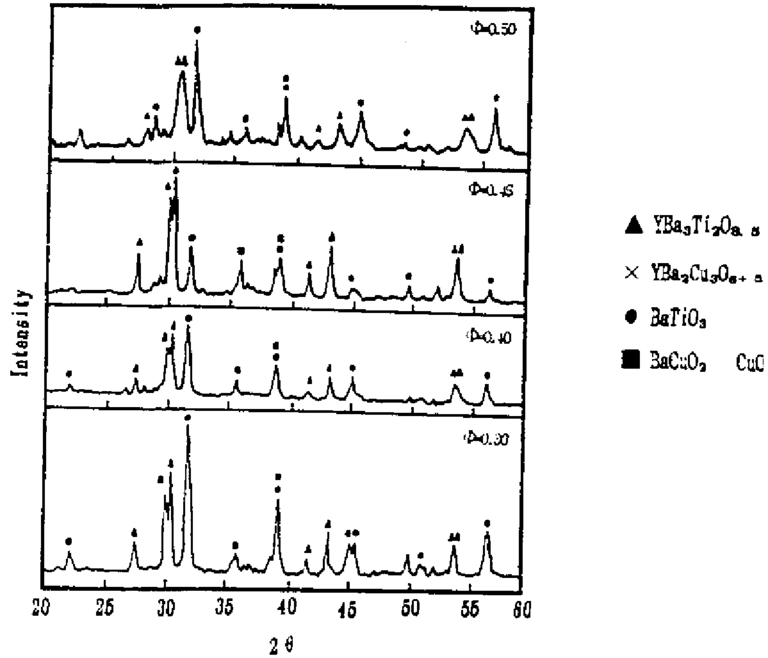

Fig 1 a) Φ=0.30, 0.40, 0.45, 0.50

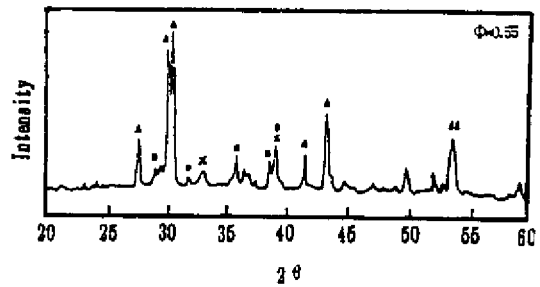

Fig 1 b) Φ=0.55

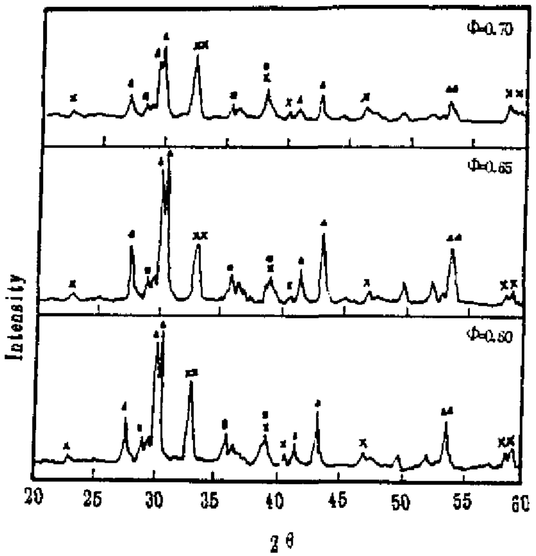

Fig. 1 c) Φ=0.60, 0.65, 0.70

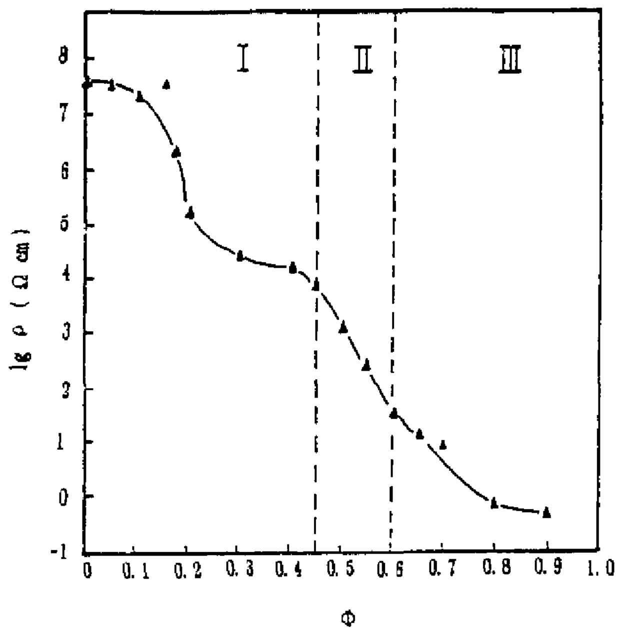

Fig.2

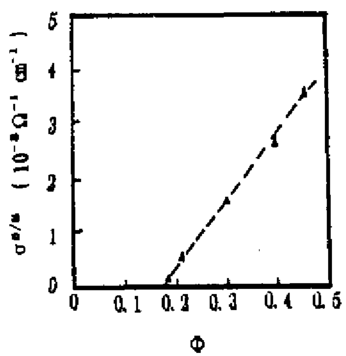

Fig.3

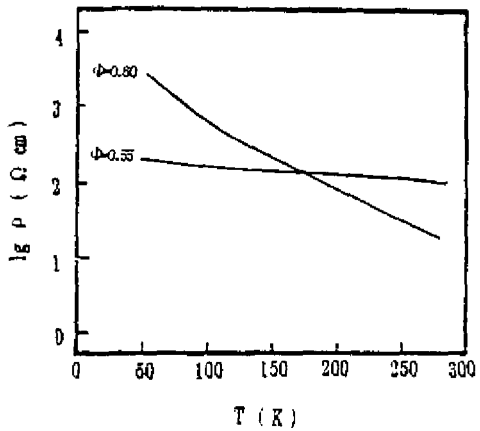

Fig.4

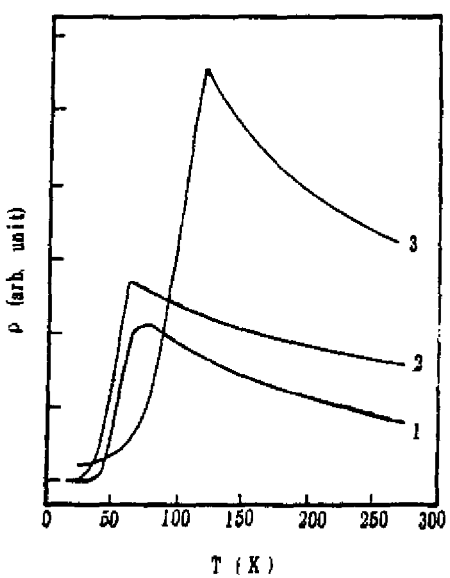

Fig.5