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A study of the $BaTiO_3$–$YBa_2Cu_3O_{6+\delta}$ ceramic composite system

Ang Chen†‡§, Yu Zhi‖, Yahua Bao‖, Xi Dai† and Qin Jiang†

† Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

‡ China Centre of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing 100080, People's Republic of China

§ International Centre for Theoretical Physics, Trieste, Italy

‖ Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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Abstract. A class of ceramic composite prepared with two kinds of oxide ceramic, namely ferroelectric $BaTiO_3$ and superconducting $YBa_2Cu_3O_{6+\delta}$, is reported, and the phase structure and electrical transport properties of the samples are investigated. The results show that the main phases varied in different composition regions. For low nominal $YBa_2Cu_3O_{6+\delta}$ contents, 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.

1. Introduction

Perovskite-type oxides have received considerable attention since the discovery of high-T_c superconducting oxide ceramics in the field of solid state physics. Rich and varied physical phenomena exist in these oxide ceramics, whose properties are closely related to their composition and structure [1,2]. For instance, high-temperature superconductivity in $YBa_2Cu_3O_{6+\delta}$ ceramics is obtained by drawing electrons from the antiferromagnetic base; 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 of the physical properties in the materials is important.

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

2. 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 $(1-\phi)BaTiO_3$–$\phi YBa_2Cu_3O_{6+\delta}$, where the volume fraction ϕ of $YBa_2Cu_3O_{6+\delta}$ is 0, 0.05,

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0.10, 0.16, 0.18, 0.20, 0.30, 0.40, 0.45, 0.55, 0.60, 0.65, 0.70, 0.80 or 0.90. The powders were weighed, mixed, dried and pressed into pellets. The pellets were then sintered at 980–1250 °C and annealed at 550 °C for 4 h in air. The sintering temperatures for the samples were decided according to the ceramic densities of the samples. The ceramic densities of all samples obtained are in the range from 5.3 to 5.5 g cm^{-3}.

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

3. Results and discussion

3.1. 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. Typical x-ray diffraction (XRD) patterns of the samples are shown in figure 1. The composition can be divided into three parts according to the XRD results.

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

(2) For higher $YBa_2Cu_3O_{6+\delta}$ contents $0.60 \leqslant \phi < 1$ (denoted as region III), the $YBa_2Cu_3O_{6+\delta}$ phase was formed; the sintering temperature for these compositions was decreased to 1050 °C for 1 h, close to the sintering temperature for the $YBa_2Cu_3O_{6+\delta}$ superconductor. The predominant phases became $YBa_2Cu_3O_{6+\delta}$ and $YBa_3Ti_2O_{8.5}$, and a little $BaCuO_2$ and CuO still exist, but $BaTiO_3$ 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 a little $YBa_2Cu_3O_{6+\delta}$, $BaTiO_3$, $BaCuO_2$ and CuO exist.

3.2. Conduction of the functional ceramic composite

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

3.2.1. The percolation conductivity in region I ($0 < \phi \leqslant 0.45$). 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 increasing content ϕ according to the above XRD results. Grains of $YBa_3Ti_2O_{8.5}$ phase were randomly incorporated into the $BaTiO_3$ matrix from the viewpoint of microstructure. The whole

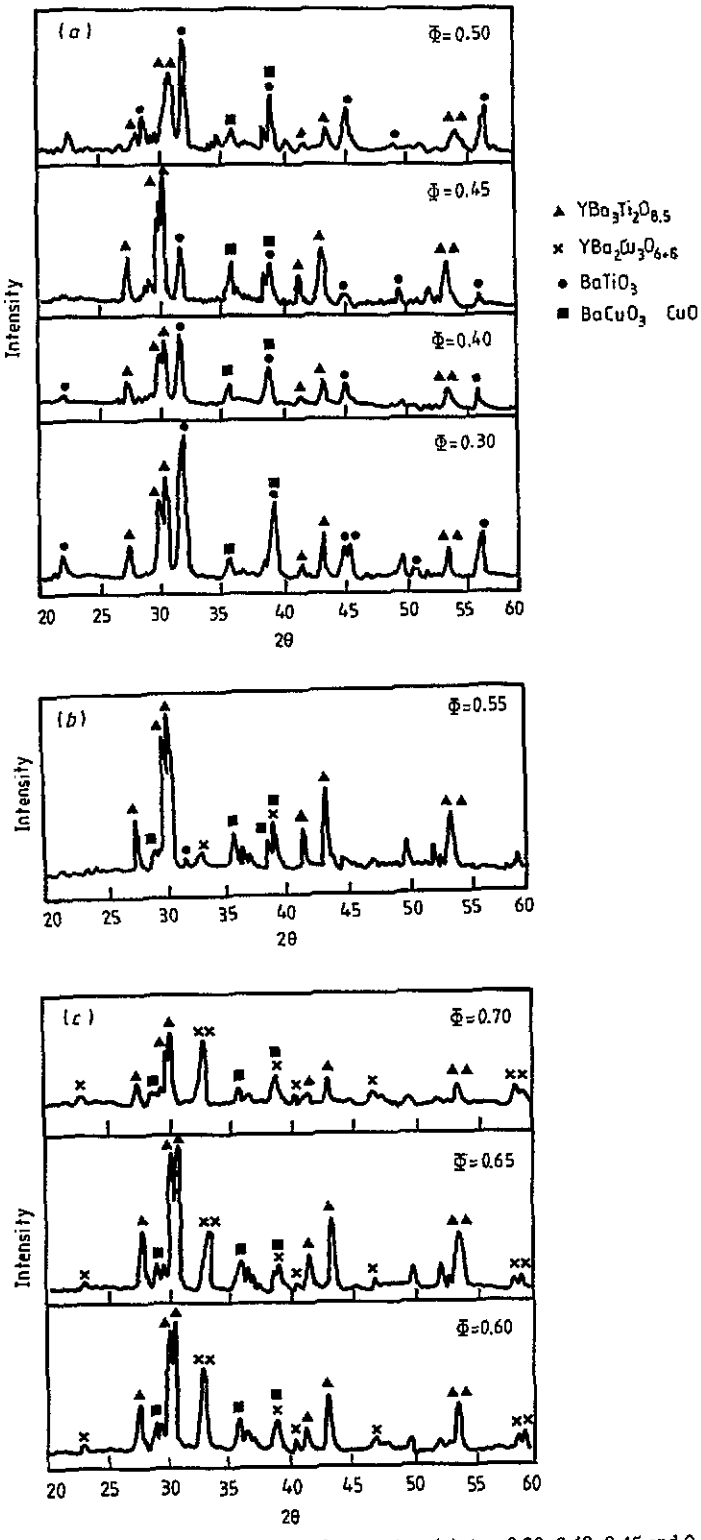

Figure 1. Typical XRD patterns of the samples: (*a*) $\phi = 0.30$, 0.40, 0.45 and 0.50; (*b*) $\phi = 0.55$; (*c*) $\phi = 0.60$, 0.65 and 0.70.

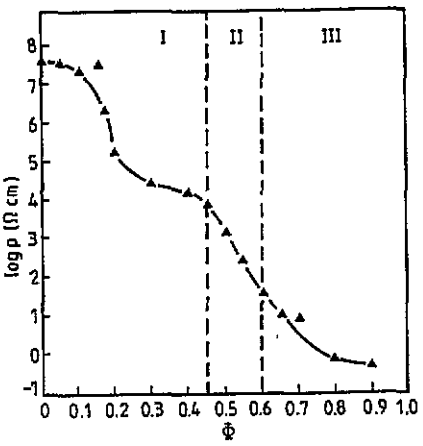

Figure 2. Composition dependence of the resistivity of the samples.

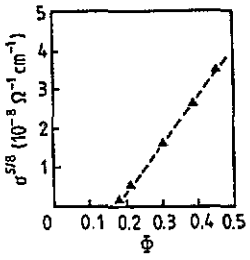

Figure 3. Plot of $\sigma^{5/8}$ versus ϕ.

resistivity is dependent upon the volume proportions and the resistivities of the two phases in the composite materials consisting of $BaTiO_3$ and $YBa_3Ti_2O_{8.5}$ phases. Figure 2 shows the composition dependence of resistivity. For $0 \leqslant \phi \leqslant 0.10$, the high resistivity of the composite indicates the high-resistivity phase $BaTiO_3$. For ϕ in a narrow range from 0.16 to 0.20, the resistivity decreases abruptly from 10^7 to 10^4 Ω cm. The percolation threshold ϕ is defined as the volume fraction at which conducting paths begin to form. That is, for $\phi < \phi_c$, the segregation of limited clusters predominates and the material cannot conduct when the volume fraction of the $YBa_3Ti_2O_{8.5}$ phase is very low; at $\phi = \phi_c$, an infinite continuous $YBa_3Ti_2O_{8.5}$ grain cluster begins to form conducting pathways and the materials conduct, resulting in low resistivity. Finally, in the range $0.20 \leqslant \phi \leqslant 0.45$, 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 $YBa_3Ti_2O_{8.5}$ phase.

From the above discussion, it is concluded that the conductivities 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 deduced that the resistivity of the $YBa_3Ti_2O_{8.5}$ phase is lower than that of the $BaTiO_3$ phase.

In a system composed of a high-conductivity phase and a low-conductivity 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]

$$\xi \sim |\phi - \phi_c|^{-\upsilon} \tag{1}$$

where ϕ is the percentage of high-conductivity 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:

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

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

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

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

i.e.

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

The $\sigma^{5/8}$ versus ϕ curve is plotted in figure 3 according to the $\log\rho$ versus ϕ curve in figure 2. The straight line in figure 3 extrapolated to $\sigma = 0$ gives the intercept $\phi_c \simeq 0.17$. This critical volume fraction is in good agreement with the theoretical value of the three-dimensional percolation threshold, 0.16 ± 0.02 [7]. This result further shows that the $YBa_3Ti_2O_{8.5}$ phase and the $BaTiO_3$ phase are randomly distributed in the ceramic composite and the influence of the secondary phase on its conductivity can be neglected.

3.2.2. 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 a little $YBa_2Cu_3O_{6+\delta}$, $BaTiO_3$, $BaCuO_2$ and CuO exist. The electrical properties of the samples mainly indicated the characteristics of the doped $YBa_3Ti_2O_{8.5}$ phase. The resistivity of samples in region II ranged from 10^2 to 10^3 Ω cm, and it is nearly independent of temperature as shown in figures 2 and 4. The electrical transport behaviour of the single $YBa_3Ti_2O_{8.5}$ phase as well as that of the doped $YBa_3Ti_2O_{8.5}$ phase need further study.

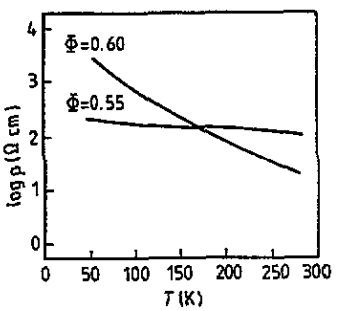

Figure 4. Temperature dependence of resistivity in the temperature range from 10 to 300 K for $\phi = 0.55$ and 0.60.

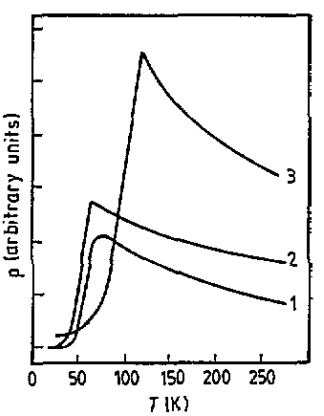

Figure 5. Temperature dependence of resistivity in the temperature range from 10 to 300 K for $\phi = 0.90$ (curve 1), $\phi = 0.80$ (curve 2) and $\phi = 0.65$ (curve 3).

3.2.3. Superconductivity in region III ($0.60 \leqslant \phi < 1$). In region III, the XRD results indicate that the ceramic composite mainly consists of $YBa_2Cu_3O_{6+\delta}$ phase and $YBa_3Ti_2O_{8.5}$ phase for $0.65 \leqslant \phi < 1$. Percolation behaviour similar to region I should have occurred, as the resistivity of the $YBa_2Cu_3O_{6+\delta}$ phase is much lower than that of the $Ba_3Ti_2O_{8.5}$ phase. In fact, the resistivity of the composites decreases almost linearly with increasing nominal content ϕ, as shown in figure 2. The measured temperature dependence of resistivity of

the composites in the temperature range from 10 to 300 K for $\phi = 0.55$, 0.60, 0.65, 0.80 and 0.90 is shown in figures 4 and 5. The resistivity of the composite material is about 10 Ω cm for $\phi = 0.6$ and it shows semiconducting behaviour at low temperatures. As the $YBa_2Cu_3O_{6+\delta}$ nominal content increases further, for $\phi = 0.8$ and 0.9, a weak negative temperature characteristic occurs initially; then at 60–70 K 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 the $YBa_2Cu_3O_{6+\delta}$ system undergoes a transition from semiconducting behaviour to metal conducting behaviour and the corresponding resistivity at room temperature decreases, as the oxygen content δ increases [3].

The temperature dependence of the resistivity together with the resistivity at room temperature in figures 2, 4 and 5 indicated that the resistivity of the composites is dependent upon that of the $YBa_2Cu_3O_{6+\delta}$ in region III. Meanwhile, it is known that the resistivity of $YBa_2Cu_3O_{6+\delta}$ depends upon the oxygen content δ [3], so it can be deduced that the variation in resistivity at room temperature and the R–T characteristics of the composite correspond to the variation in the oxygen content of $YBa_2Cu_3O_{6+\delta}$ in the composites. For instance, for low nominal $YBa_2Cu_3O_{6+\delta}$ contents, the higher resistivity of composites possibly corresponds to the higher resistivity of $YBa_2Cu_3O_{6+\delta}$ with the lower oxygen content δ in the composites; the decrease in the resistivity of the composites corresponds to the decrease in the resistivity of $YBa_2Cu_3O_{6+\delta}$, which is possibly due to the increase in oxygen content δ of $YBa_2Cu_3O_{6+\delta}$ in composites with increasing proportion of $YBa_2Cu_3O_{6+\delta}$ phase. In region III, percolation behaviour similar to region I does not occur, although the resistivity of the $YBa_2Cu_3O_{6+\delta}$ phase is much lower than that of the $YBa_3Ti_2O_{8.5}$ phase. This behaviour is attributed to the change in the resistivity of the $YBa_2Cu_3O_{6+\delta}$ phase in the whole composition range of region III.

The present work shows that a mechanical mixture of two kinds of functional ceramic is obtained by means of an appropriate manufacturing process; rich and varied physical phenomena exist 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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References

[1] Chen Ang, Zhi Yu, Li Biaorong, Wang Shaojie and Chen Yilong 1992 *J. Phys.: Condens. Matter* **4** 4981
Chen Ang, Zhi Yu, Li Biaorong and Wang Shaojie 1992 *Phys. Lett.* **165A** 171
[2] Chen Ang and Zhi Yu 1992 *J. Appl. Phys.* **71** 4451, 6025
[3] Ginsberg D M (ed) 1989 *Physical Properties of High Temperature Superconductors I, II* (Singapore: World Scientific)
[4] Shooley J E, Hosler W R and Cohen M L 1964 *Phys. Rev. Lett.* **12** 474
Chen Ang and Zhi Yu 1991 *Chinese Phys. Lett.* **8** 129, 132
[5] Lark R F and Chamis C C 1986 *J. Compos. Technol. Res.* **8** 3
[6] Kinner M K 1980 *Mater. Eng.* **91** 1
[7] Shante V K S and Kirkpatrick S 1971 *Adv. Phys.* **22** 325