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## Variable-range-hopping conduction and metal–insulator transition in Cu-doped BaTiO<sub>3</sub>

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**Abstract.** Cu-doped BaTiO<sub>3</sub> polycrystals with the nominal composition of Ba(Ti<sub>1-x</sub>Cu<sub>x</sub>)O<sub>3-δ</sub> ( $x = 0.1-1$ ) were synthesized. The samples are multiphase. The metallic conducting behaviour was seen for the sample with  $x = 0.5$ , while semiconducting behaviour appears for the other compositions. For  $x = 0.4$ , variable-range-hopping conduction was observed. The results are briefly discussed. It is proposed that the BaTiO<sub>3</sub> phase modified by Cu doping might be responsible for the metallic behaviour observed.

### 1. Introduction

Pure 3d<sup>0</sup> SrTiO<sub>3</sub> is a typical band insulator with a wide band gap of 3.2 eV. However, doping with Nb or introducing oxygen vacancies in SrTiO<sub>3</sub> leads to metallic behaviour and even superconductivity [1]. Recently, Suzuki, *et al* [2] reported that La doping also caused superconductivity in SrTiO<sub>3</sub>. Some of the present authors observed a variable-range-hopping (VRH) conduction in SrTiO<sub>3</sub> doped with Fe [3].

Like SrTiO<sub>3</sub>, pure 3d<sup>0</sup> BaTiO<sub>3</sub> is an insulator with the energy gap of 3 eV [4]. Interestingly, the question has been raised of whether BaTiO<sub>3</sub> could be induced to show metallic behaviour by doping with an impurity or introducing oxygen vacancies.

In 1955, Haayman *et al* [5] discovered an interesting semiconducting behaviour in doped BaTiO<sub>3</sub>—the so-called positive-temperature-coefficient effect—which shows a drastic rise in resistance in the vicinity of the Curie temperature. Since then, the semiconducting behaviour of BaTiO<sub>3</sub> doped with a small amount of impurity has been extensively studied [5–15]. However, the physical mechanism of the conduction in semiconducting BaTiO<sub>3</sub> is still a subject of controversy. No conclusion has been reached as to whether the carriers are small polarons [7, 8, 11] or conduction electrons [2, 6].

Recently, Akishige *et al* [16–18] reported that a metal–insulator (M–I) transition occurs in both cubic and hexagonal BaTiO<sub>3</sub> under high pressure (higher than 2.3 GPa) at cryogenic temperatures. In addition, although Ba-doped LaTiO<sub>3</sub> solid solution, (La<sub>1-x</sub>Ba<sub>x</sub>)TiO<sub>3</sub> ( $x \leq 0.5$ ), shows a metallic behaviour at cryogenic temperatures, the metallic behaviour was considered to be due to the contribution from the metallic LaTiO<sub>3</sub> [19, 20]. To date, to the authors' knowledge, no work has been reported concerning the examination of whether the metallic conduction behaviour occurs in impurity-doped BaTiO<sub>3</sub> at cryogenic temperatures.

It is known that the transition-metal Cu ions play a unique role in a series of high- $T_c$  superconductors. On the other hand, Cu ions can be used to modify the dielectric properties of  $\text{BaTiO}_3$  [21]. In this work, we choose the element Cu to use in studying the effect of doping on the electrical transport behaviour of  $\text{BaTiO}_3$ . We have observed both the M–I transition and VRH conduction in Cu-modified  $\text{BaTiO}_3$  multiphase polycrystals.

## 2. Experimental procedure

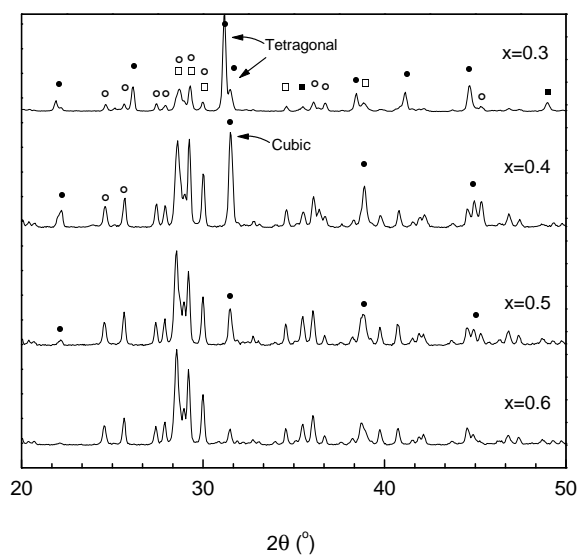
Cu-doped  $\text{BaTiO}_3$  polycrystals with the nominal composition  $\text{Ba}(\text{Ti}_{1-x}\text{Cu}_x)\text{O}_{3-\delta}$  ( $x = 0.1-1$ ) were prepared by solid-state reaction. In order to compare the resistivity behaviour of the samples,  $\text{Ba}_2\text{TiO}_4/\text{BaCuO}_2$  composites were also synthesized. The raw materials  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{CuO}$  were mixed and calcined at  $900^\circ\text{C}$  for one hour. The calcined powders were pressed into pellets and sintered at  $1000-1200^\circ\text{C}$  for one hour in air.

The phases of the samples were examined by x-ray powder diffraction (XRD). The resistivity of the samples was measured with a Keithley-617 Electrometer over the temperature range  $45\text{ K}-300\text{ K}$  in a cryogenic system, while the temperature of the samples was changing at a rate of  $1\text{ K}$  per minute, and data were taken every  $1$  or  $2\text{ K}$ . Gold or In–Ga alloy was used for the electrodes.

## 3. Results and discussion

### 3.1. Phases and conduction behaviour of $\text{Ba}(\text{Ti}_{1-x}\text{Cu}_x)\text{O}_3$ compositions

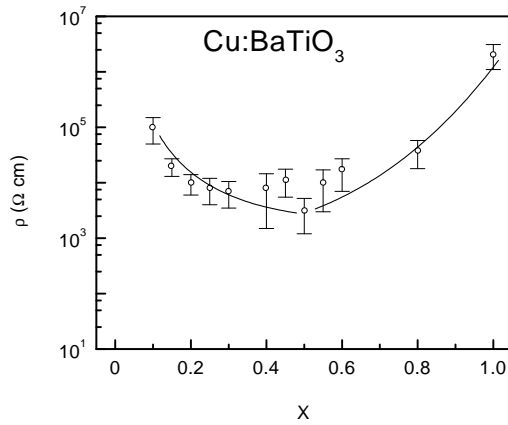
The results of XRD analysis indicate that all of the samples are multiphase. Typical XRD patterns for the  $\text{Ba}(\text{Ti}_{1-x}\text{Cu}_x)\text{O}_{3-\delta}$  samples with  $x = 0.3, 0.4, 0.5$  and  $0.6$  are shown in figure 1. For  $x = 0.3$  and  $x = 0.4$ , the samples are mainly composed of  $\text{BaTiO}_3$  and  $\text{BaCuO}_2$  phases, with small amounts of  $\text{Ba}_2\text{TiO}_4$  and  $\text{CuO}$  phases. For  $x = 0.5$  and  $0.6$ , there are



**Figure 1.** XRD patterns of  $\text{Ba}(\text{Ti}_{1-x}\text{Cu}_x)\text{O}_{3-\delta}$  ( $x = 0.3, 0.4, 0.5$  and  $0.6$ ) multiphase ceramics: (solid circles)  $\text{BaTiO}_3$ , (open squares)  $\text{BaCuO}_2$ , (open circles)  $\text{Ba}_2\text{TiO}_4$  and (solid squares)  $\text{CuO}$ .

three main phases: Ba<sub>2</sub>TiO<sub>4</sub>, BaCuO<sub>2</sub> and BaTiO<sub>3</sub>, with a small amount of CuO phase. From figure 1, it can be seen that the BaTiO<sub>3</sub> phase is tetragonal in the sample with  $x = 0.3$ ; however, it becomes cubic for  $x = 0.4, 0.5$  and  $0.6$ . This implies that with increasing Cu concentration, the crystalline structure of the BaTiO<sub>3</sub> phase is modified.

The resistivity ( $\rho$ ) of the Ba(Ti<sub>1-x</sub>Cu<sub>x</sub>)O<sub>3- $\delta$</sub>  samples was measured at room temperature, and the results are shown in figure 2. The error bars show a distribution of the resistivity for the samples from different batches. The results show that the resistivity of the samples depends, to some extent, on the preparation processes. However, it can be seen that the variation of the resistivity values is within a distribution limit and shows the same overall tendency with varying Cu concentration. The resistivity decreases with increasing Cu concentration and exhibits a minimum value of  $(1-3) \times 10^3 \Omega \text{ cm}$  at about  $x = 0.4-0.5$ . With further increase in Cu concentration, the resistivity increases. In addition, it should be pointed out that the resistivity can be changed by exposure to humid environments, indicating that the samples are not very stable.



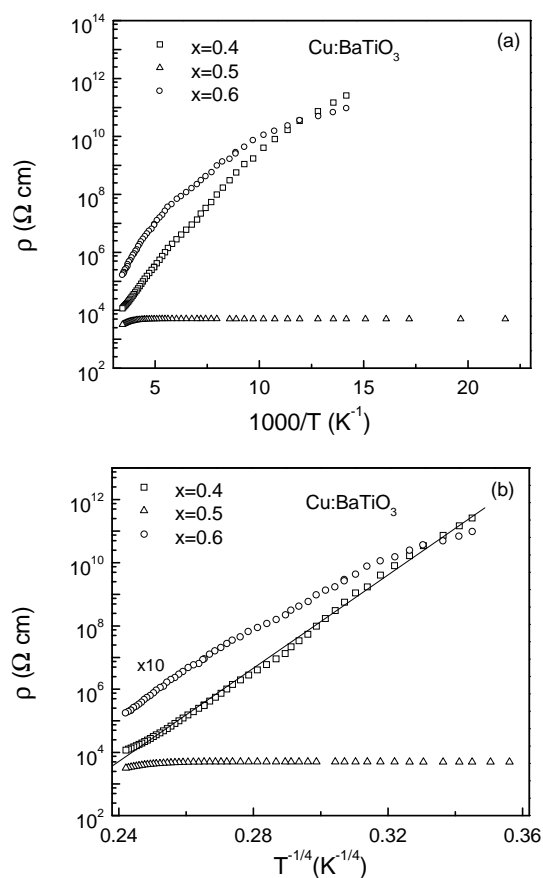
**Figure 2.** The room temperature resistivity ( $\rho$ ) of Ba(Ti<sub>1-x</sub>Cu<sub>x</sub>)O<sub>3- $\delta$</sub>  multiphase ceramics as a function of the Cu content  $x$ . Note that the error bars indicate the distribution of the resistivity for the four batches of samples for each composition, not experimental error.

The temperature dependence of the resistivity of the Ba(Ti<sub>1-x</sub>Cu<sub>x</sub>)O<sub>3- $\delta$</sub>  ( $x = 0.4, 0.5, 0.6$ ) samples is shown in figure 3. The resistivity of the samples with  $x = 0.4$  and  $0.6$  decreases with increasing temperature, exhibiting semiconducting behaviour. However, for the sample with  $x = 0.5$ , metallic behaviour of the resistivity is observed. For  $x = 0.4$  and  $0.6$ , the resistivity at low temperatures is so large that the measurements are only valid up to 70 K.

The semiconducting behaviour of the resistivity,  $\rho \sim 1/T$  in figure 3(a) cannot be fitted to the thermally activated conduction,  $\rho = \rho_0 \exp[U/(k_B T)]$ . However, it can be seen from figure 3(b) that the experimental data for  $x = 0.4$  in the temperature range 70–291 K fit well to the VRH conduction expression [22, 23]:

$$\rho = \rho_0 \exp[(T_0/T)^{1/4}]. \quad (1)$$

In this model, it is assumed the charge carriers move away along a path determined by the optimal rate of pair hopping from one localized state to another. Band conduction is absent because the extended states are far away from the Fermi level. The fit parameter  $T_0 = 8.3 \times 10^8 \text{ K}$  was obtained; the high  $T_0$ -value is similar to that of La<sub>2</sub>CuO<sub>4</sub> doped to a high Li concentration [24].



**Figure 3.** The temperature dependences of the resistivities ( $\rho$ ) of  $\text{Ba}(\text{Ti}_{1-x}\text{Cu}_x)\text{O}_{3-\delta}$  multiphase ceramics with  $x = 0.4, 0.5$  and  $0.6$ : (a)  $\rho$  versus  $1/T$ ; (b)  $\rho$  versus  $1/T^{1/4}$ ; the solid line is the fit to equation (1).

For  $x = 0.6$ , the resistivity does not simply follow equation (1), and it seems that the properties of the sample may be influenced by both the VRH conduction and the thermally activated conduction. This implies that with further increasing Cu concentration, the sample becomes re-localized.

Semiconducting conduction via the VRH mechanism and metallic behaviour are observed, i.e., a M–I transition occurs in  $\text{Ba}(\text{Ti}_{1-x}\text{Cu}_x)\text{O}_{3-\delta}$  with variation of the Cu concentration. Similarly, VRH behaviour and a M–I transition were observed in a series of oxides,  $\text{La}_2\text{CuO}_4$  [24, 25],  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  [26],  $\text{YBaCuO}$  [27, 28] and  $\text{Sr}(\text{Ti}, \text{Fe})\text{O}_3$  [3]. This seems to imply that it is very possible that the occurrence of VRH is a precursor of the M–I transition in some oxides.

### 3.2. Phases and conduction behaviour of $\text{BaTiO}_3$ – $\text{BaCuO}_2$ compositions

As Cu-doped  $\text{BaTiO}_3$  is a multiphase system, it is important to establish which phase is responsible for the metallic conduction behaviour. The XRD results indicate that the sample with  $x = 0.5$ , showing metallic behaviour, is mainly composed of  $\text{Ba}_2\text{TiO}_4$ ,  $\text{BaCuO}_2$  and

BaTiO<sub>3</sub>. In order to determine whether the metallic conducting behaviour arises from the Ba<sub>2</sub>TiO<sub>4</sub> and BaCuO<sub>2</sub> phases, a series of composite samples, (1 - y)Ba<sub>2</sub>TiO<sub>4</sub>-yBaCuO<sub>2</sub> (y = 0.1, 0.3, 0.5 and 0.6), were prepared. The XRD results show that all of the samples are composed of the Ba<sub>2</sub>TiO<sub>4</sub> and BaCuO<sub>2</sub> phases. The resistivity of the samples at room temperature is in the range 10<sup>5</sup> to 10<sup>6</sup> Ω cm, which is higher than that for the Ba(Ti<sub>1-x</sub>Cu<sub>x</sub>)O<sub>3-δ</sub> samples. In addition, semiconducting behaviour of the resistivity with thermally activated conduction was observed for the (1 - y)Ba<sub>2</sub>TiO<sub>4</sub>-yBaCuO<sub>2</sub> system. These results indicate that the diphasic system Ba<sub>2</sub>TiO<sub>4</sub>/BaCuO<sub>2</sub> does not contribute to the metallic behaviour.

### 3.3. Discussion

The existence of the resistivity minimum (figure 2) implies that there must exist one phase whose resistivity is equal to or less than (1-3) × 10<sup>3</sup> Ω cm. However, it is known that, at room temperature, the resistivities of pure BaTiO<sub>3</sub> and pure Ba<sub>2</sub>TiO<sub>4</sub> are higher than 10<sup>10</sup> Ω cm and the resistivity of BaCuO<sub>2</sub> is higher than 10<sup>6</sup> Ω cm. From the results in section 3.2, the conclusion can be drawn that the diphasic system Ba<sub>2</sub>TiO<sub>4</sub>/BaCuO<sub>2</sub> makes no contribution to the metallic behaviour observed.

In this work, the XRD results show that the BaTiO<sub>3</sub> phase is distorted and its crystal structure changes from tetragonal to cubic as x increases from x ≤ 0.3 to x ≥ 0.4. It can therefore be expected that Cu ions will partially substitute for the Ti sites. In addition, it is well known that the high-T<sub>c</sub> superconducting oxide YBCO is influenced by the preparation process due to the variation of the oxygen content. In the present work, the electrical conduction behaviour depends to some extent on the preparation process; this implies that the oxygen vacancies also play an important role in the Cu-doped BaTiO<sub>3</sub> system. Considering that oxygen-deficient cubic and hexagonal BaTiO<sub>3</sub> exhibit metallic behaviour under high pressure [16–18], it is reasonable to assume that the BaTiO<sub>3</sub> phase modified by Cu ions is responsible for the metallic behaviour observed in this work—i.e., for the sample with x = 0.5, some Cu ions enter the lattice of the BaTiO<sub>3</sub> phase (very probably, the oxygen content changes simultaneously). This leads to an effect on the electrical conduction equivalent to those in the cases of cubic and hexagonal BaTiO<sub>3</sub> under high external pressure. The electronic structure of BaTiO<sub>3</sub> is modified, and hence metallic behaviour occurs. However, upon further increase of the Cu concentration, to x ≥ 0.6, the samples are re-localized. This implies that the metallic behaviour only occurs under certain favourable conditions, such as (in the present case) for x = 0.5. At this stage, a clear understanding is lacking and further work is needed.

## 4. Conclusions

In conclusion, metallic conducting behaviour was observed for the nominal composition Ba(Ti<sub>1-x</sub>Cu<sub>x</sub>)O<sub>3-δ</sub> with x = 0.5; however, semiconducting behaviour appears for the other compositions. For x = 0.4, the VRH mechanism was observed. The metallic behaviour probably arises from the Cu-modified BaTiO<sub>3</sub> phase. Unfortunately, we cannot establish at present a single phase that is responsible for the metallic conducting behaviour. However, we hope that the results reported here will attract more attention to the transport behaviour of doped BaTiO<sub>3</sub> at low temperatures.

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