Research Article

Preparation and Characterization of Ag-Doped BaTiO₃ Conductive Powders

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BaTiO₃ powders doped with Ag at different Ag/Ba molar ratios were prepared by sol-gel method. The resistivity reached the lowest point of 5.644 Ω·m when Ag concentration was 0.10 at% and the powders were calcined for two times at 800°C and 500°C. XRD and FTIR investigations showed that no new substance was formed after the doping and calcining process, but the particle size and the strength of Ti-O bond in modified BaTiO₃ crystal cell all changed. The conductivity of Ag-doped BaTiO₃ powders with different Ag concentrations and through different preparing methods was discussed by using defect theory.

1. Introduction

Conductive powders are promising materials applied as film conductors [1–3]. It is also used as conductive fillers in polymers to make it electrically conductive, resistant to static electricity and to screen electromagnetic wave [4]. There are many series of conductive powders such as carbon, metals, and ceramics [5].

BaTiO₃ with a perovskite structure is noteworthy for its exceptional dielectric, piezoelectric, electrostrictive, and electrooptic properties with corresponding electronic applications [6–8]. Various studies have been performed to obtain BaTiO₃ of better electronic properties by doping different elements [9–12]. In order to obtain BaTiO₃ of low resistivity, Zhao [13] doped Ag⁺ into BaTiO₃ and conductive ceramics of $\rho \approx 28 \Omega \cdot \text{m}$ were prepared. Wu et al. [14] studied the influences on conductivity of doping different rare-earth elements into BaTiO₃. Hao prepared BaTiO₃ ceramics doped with Nb₂O₃ [15], Sm₂O₃ [16], Gd₂O₃ [17], and La³⁺ [18] (by gaseous penetration method) and achieved resistivity of $\rho = 2.364 \times 10^8 \Omega \cdot \text{m}$, $2.1 \times 10^2 \Omega \cdot \text{m}$, $1.27 \times 10^5 \Omega \cdot \text{m}$, and $8.2 \times 10^4 \Omega \cdot \text{m}$, respectively. Because the raw materials for synthesizing BaTiO₃ are relatively cheap, to make the powders semiconductive by doping different ions into BaTiO₃ seems to be not only a feasible but also a promising way to satisfy the needs for the application of conductive powders.

In this paper, BaTiO₃ powders doped with Ag were synthesized and low resistivity of such powders is reported. Their electrical and compositional characteristics are measured and studied.

2. Experiments

2.1. Preparation of BATO Powders. The Ag-doped BaTiO₃ powders (BATO) were prepared by sol-gel method [15, 19]. Ba(Ac)₂ and Ti(OC₄H₉)₄ were used as the starting materials. Dopant was chosen to be Ag in the form of AgNO₃. The pH of the solution was adjusted to be 3.5 by adding glacial acetic acid. Gels were prepared through standard sol-gel procedure. The gel powders were calcined at 800°C for 2 h and then were calcined at 500°C for 2.5 h for the second time (SCalcination). Here the SCalcination method is an effective way to decrease the resistivity of BATO powders.

2.2. Analysis. The resistivity of the BATO powders was determined by using a standard four-point method (Keithley's SourceMeter, model 2400, America). Structural analysis was performed by X-ray diffraction analysis (Seifert Debye Flex 2002). Fourier Transform Infrared spectroscopic measurements were performed by using an IR spectrophotometer (Nicolet AVATAR 320, America) ranging from 450 to 4000 cm⁻¹.

TABLE 1: Electric resistivity of BATO powders before and after SCalcination ($\Omega \cdot m$).

Process	$n(\text{Ag}) : n(\text{Ba})$				
	0.0005	0.0010	0.0015	0.0020	0.0025
Pro-SCalcination	146.47	102.43	1821.04	2849.88	260.35
Post-SCalcination	72.39	5.64	7.18	8541.82	2113.58

3. Results and Discussion

3.1. Electric Properties of BATO Powders. The electric resistivity of BATO powders at different Ag concentrations is shown in Table 1. The influence of the second calcination at 500°C after the calcination at 800°C (SCalcination) on the resistivity can be seen in Figure 1.

The resistivity of undoped BaTiO₃ powder is $4.0 \times 10^9 \Omega \cdot m$ and is not shown in Table 1 or Figure 1.

It can be seen that as Ag concentration increased, the resistivity at first decreased, followed by an increase and another decrease. Such flat S-shaped trend was complied by the resistivity of both of pre- and post-SCalcination. The difference between the two processes is that SCalcination decreased the resistivity of BATO powders from the Ag/Ba molar ratio of 0.0005 to 0.0015, while it increased the resistivity at 0.0020 and 0.0025. The resistivity after SCalcination decreased the most at the Ag concentration of 0.15 at%, from 1821.04 $\Omega \cdot m$ to 7.18 $\Omega \cdot m$.

3.2. XRD Analysis of BATO Powders. Figure 2 gives the XRD patterns. It can be concluded that no new substance was formed during the doping or calcination process other than BaTiO₃ and BaCO₃. It is also found that doping Ag and SCalcination both contribute to minimize the second phase and obtain purer BATO samples. The peaks in XRD patterns slightly changed their positions after doping and after SCalcination. The strongest diffraction of the sample 1[#] (undoped BaTiO₃) is at 31.44°, while in 2[#] at 31.46° and 3[#] at 31.52°. The shift of BaTiO₃ peaks showed that Ag entered BaTiO₃ crystal lattice, leading to the increase of the conductivity of the powders.

The particle size of BATO powders was calculated using Scherrer Formula and FWHM of (200) reflection observed via the X-ray data. The particle size of sample 1[#] is calculated to be 11.81 nm, while the particle sizes of sample 2[#] and 3[#] are 20.31 nm and 18.29 nm, respectively. In other words, we can see that the particle size was increased after doping but reduced after the SCalcination.

3.3. FTIR Spectra Analysis. The FTIR spectra of samples 1[#], 2[#], and 3[#] are shown in Figure 3.

The characteristic absorption at 3410 cm⁻¹ is assigned to -OH stretching vibration, due to the water brought by KBr or absorbed on the powder surface. The characteristic absorption at 1440 cm⁻¹ is assigned to the stretching vibrations of carboxylate. This is because there is a small amount of BaCO₃ in the samples, which is in agreement with the XRD patterns. All three samples exhibit strong absorptions around 550 cm⁻¹ and 450 cm⁻¹, which can be assigned to the stretching and bending vibrations of the

Ti-O bond in [TiO₆]²⁻ octahedron. It is also a characteristic absorption of BaTiO₃. But the wave number of the strongest absorption around 550 cm⁻¹ varied slightly for the three samples: 547.8 cm⁻¹ for sample 1[#], 551.8 cm⁻¹ for sample 2[#], and 565.7 cm⁻¹ for 3[#]. Since the wave number increases when infrared light of higher frequency and thus stronger energy is absorbed, it can be concluded that the Ti-O bond was strengthened after the doping and further strengthened after SCalcination.

3.4. Discussions on the Resistivity of BATO. During the calcination process AgNO₃ decomposed into Ag₂O, which entered BaTiO₃ lattice. Since Ag⁺ possesses only one positive charge and Ba²⁺ possesses two, the substitution must be charge-compensated to maintain charge neutrality. According to the defect theory established by Kroger and Vink forty years ago, the incorporation of Ag₂O as an acceptor dopant can be written as (1) to (3):

Since the perovskite structure is relatively a close packed one, the formation of interstitial ions is not as easy as the formation of vacancy. So the incorporation of Ag₂O would prefer the way presented in (1).

The formation of oxygen vacancy can be proved by the FTIR result, in which the wave number of the characteristic absorption of Ti-O bond changed among the three samples. As stated previously, the strength of Ti-O bond in the [TiO₆]²⁻ octahedron was stronger in the sample doped with Ag than the undoped BaTiO₃ sample. It can be explained as that, since the formation of oxygen vacancies means that there is O²⁻ leaving the cell, the [TiO₆]²⁻ octahedron was distorted and Ti⁴⁺ gained a stronger attraction of the O²⁻ left, rendering the Ti-O bond stronger.

The oxygen vacancy formed was in equilibrium with the formation of hole:

So that is the ultimate reason why doping AgNO₃ would render BaTiO₃ semiconductive.

As is shown in Figure 1(a), increasing AgNO₃ will decrease resistivity because the conductivity is proportional to the concentration of oxygen vacancy. However we should also be aware that a high concentration of defect would distort the crystal structure thus undermining conductivity.

FIGURE 1: The comparison of the resistivity of BATO powders between (a) pro-SCalcination and (b) post-SCalcination.

FIGURE 2: XRD patterns of the BaTiO₃ powders doped with Ag (1[#]) undoped BaTiO₃; (2[#]) BATO with Ag concentration of 0.15 at%; (3[#]) after the calcination at 500°C for 2.5 h.

Such two factors together influence the conductivity and resulted in the trend of conductivity change before Ag concentration of 0.15 at% in Figure 1(a).

However the following drop of resistivity at Ag concentration of 0.20 at% and 0.25 at% may result from the formation of silver during the drop of temperature in the cooling process after calcination of the BATO powders. The silver would remain in the grain boundary and serve as a good conductor, reducing the grain boundary resistivity. Since the total resistivity of BaTiO₃ is composed of grain resistivity and grain boundary resistivity, the overall resistivity is reduced. This explains the drop of resistivity after Ag concentration of 0.15 at% in Figure 1(a).

To explain the conductivity trend presented in Figure 1(b), we must first understand that not all the AgNO₃

FIGURE 3: FTIR spectrum of BATO powders: (1[#]) undoped BaTiO₃; (2[#]) BATO with Ag concentration of 0.15 at%; (3[#]) after the calcination at 500°C for 2.5 h.

doped in BaTiO₃ proceeded by (1); part of Ag⁺ followed the path in (2) and (3). It is the part of Ag that occupied Ba site that formed the oxygen vacancy and thus contributed to the conductivity. So the more Ag entering Ba sites, the lower the resistivity is. Since heating provides ions with more energy to satisfy defect formation energy, SCalcination facilitated more Ag to move from interstice to Ba site. This can be proved by the calculation result of grain size that the cell size is smaller after SCalcination than before, because interstitial Ag⁺ destabilized the crystal and increased its size.

However at higher Ag concentrations (0.20 at% and above) the resistivity is higher after SCalcination than before. This may be due to two reasons. Firstly, as discussed previously, when the concentration of defect mounts to certain level, it will damage the conductivity. So SCalcination would worsen such process. Secondly, SCalcination would oxidize the silver formed during the cooling process after the first calcination.

4. Conclusions

BATO conductive powders were prepared by sol-gel method. The lowest resistivity of $\rho = 5.644 \Omega \cdot \text{m}$ was obtained when $n(\text{Ag}) : n(\text{Ba}) = 0.0010$ and after the powder was processed by calcination at 800°C for 2 h for the first time and 500°C for 2.5 h for the second time.

XRD and FTIR investigations and measurements of electric conductivity combined proved that Ag⁺ entered the lattice of BaTiO₃ and substituted for Ba²⁺, forming oxygen vacancies, which are the main reasons for the semiconductivity.

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