

# Modification of Ag-doped BaTiO<sub>3</sub> powders through La gaseous penetration route

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**Abstract:** The Ag-doped BaTiO<sub>3</sub> (BATO) polycrystalline powders were fabricated by Sol-Gel method. Further modification by rare earth La was done through gaseous penetration route. Changes in constitution, structure, and electrical conductivity before and after modification of Ag and La were characterized. The acceptor dopant Ag owned the ability to decrease the resistivity of the doping samples from  $4.30 \times 10^9 \Omega \cdot \text{m}$  to  $6.14 \times 10^5 \Omega \cdot \text{m}$  where the resistivity fell by 4 orders of magnitude when the Ag doping ratio was 0.10%. And more doping of Ag enhanced the resistivity dramatically even beyond  $2.0 \times 10^7 \Omega \cdot \text{m}$ . Yet, gaseous penetration of La successively reduced the resistivity of BATO to the lowest point of  $2.45 \times 10^5 \Omega \cdot \text{m}$ . XRD analysis indicated that the doping process of Ag did not change the perovskite structure and main phases of the powders. However, new compound BaLa<sub>2</sub>O<sub>4</sub> generated from complex reactions during the penetration process, which manifested that La<sup>3+</sup> penetrated into the crystal lattices in the form of substituting the Ti<sup>4+</sup> site. And this substitution strengthened the Ti–O bond, which led to the inhibition of blue shift in FTIR spectrum caused by doping of Ag. The morphology of La penetrated BATO powders detected by SEM and EDAX suggested that La did penetrate into the powders and this penetration process progressed the partly sintering of the powders which is in favor of the conductivity.

**Keywords:** gaseous penetration; barium titanate; rare earths; electrical conductivity

Attentions have been focusing on the electrical conductive ceramics since the PTCR effect was discovered on the semi-conducting BaTiO<sub>3</sub>(BTO) material<sup>[1–3]</sup>. Effects of doping behavior on the electrical properties of perovskite type materials were characterized by the researches domestically and internationally<sup>[4–6]</sup>. Zhang et al.<sup>[7]</sup> reported the doping effects of donor, acceptor, and donor-acceptor codoping on the electrical properties of Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> thin films, which indicates that codoped samples own much better performances. Kojima et al.<sup>[8]</sup> fabricated the BaTiO<sub>3</sub>/Ag composites by uniform Ag-deposited BaTiO<sub>3</sub> particles, which reveals the higher Vickers hardness and dielectric constant. However, few reports were related to the electrical conductivity of the acceptor doped BaTiO<sub>3</sub> ceramic powders. In this paper, the effects on the conductivity and structure of BaTiO<sub>3</sub> powders which was doped by Ag and further modified by La via a new kind of processing at gaseous state were studied. The gaseous penetration of rare earth to functional ceramics was firstly cited by Hao et al.<sup>[9,10]</sup>. This new modification route owns the merits of high effectiveness, uniformity, and maneuverability, which is contribute to the fabrication of functional ceramics.

## 1 Experimental

### 1.1 Preparation of Ag doped BaTiO<sub>3</sub> powders

Through sol-gel method, Ag-doped BaTiO<sub>3</sub> (BATO) were prepared from Ba(Ac)<sub>2</sub>, Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, and AgNO<sub>3</sub>. The pH

of the solution was adjusted to 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 yellowish BATO powders were obtained.

### 1.2 Modification of BATO powders via gaseous penetration of La

The cementation furnace was used as the basic furniture for penetration. The penetration process can be divided into three steps. First, the cementation furnace was preheated to reaction temperature and the methanol agent was dropped into the furnace to expel the air in it; second, the samples were put in the cementation furnace rapidly; finally, the home-made rare earth La agent with the concentration of 3 wt.% was dropped into the furnace and the furnace temperature was kept at 920 °C for 4.5 h.

### 1.3 Analysis on the samples

The resistivity of the modified ceramic powders was determined by using a standard four-point method (Keithley's SourceMeter, model 2400, America) after tableting. The structure of the samples was measured by the X-ray diffractometer (XRD, Cu K $\alpha$ , D/mar- $\gamma$  $\beta$ , Japan) with a graphite monochromator, 20 kV, 50 mA, DS 1°, SS 1°, RS 0.15 mm. The superficies and energy spectrum of the samples were detected by the scanning electron microscopy (SEM, Philips's FEI Sirion, Holland) with the scanning voltage is 20 kV. Fourier Transform Infrared (FTIR) spectroscopic measure-

ments of the conductive powders were performed by using an IR spectrophotometer (Nicolet AVATAR 320, America) ranging from 450–4000 cm<sup>-1</sup>.

## 2 Results and discussion

### 2.1 Electrical conductivity of La penetrated BATO powders

The determined resistivity of BATO and La penetrated BaTiO<sub>3</sub>(LBATO) powders at room temperature is listed in Table 1.

**Table 1 Resistivity of Ag-La co-modified BaTiO<sub>3</sub> powders**

Parameters	0	1	2	3	4	5
Ag doping ratio/at. %	0	0.05	0.10	0.15	0.20	0.25
BATO/(Ω·m)	4.30×10 <sup>9</sup>	9.64×10 <sup>6</sup>	6.14×10 <sup>5</sup>	2.00×10 <sup>7</sup>	2.00×10 <sup>7</sup>	2.00×10 <sup>7</sup>
LBATO/(Ω·m)	4.32×10 <sup>5</sup>	1.10×10 <sup>7</sup>	2.45×10 <sup>5</sup>	1.87×10 <sup>6</sup>	1.76×10 <sup>6</sup>	4.84×10 <sup>6</sup>

It can be seen from the detection results of electrical conductivity that the acceptor dopant Ag owns the ability to decrease the resistivity of BATO from 4.30×10<sup>9</sup> Ω·m to 6.14×10<sup>5</sup> Ω·m where the resistivity falls by 4 orders of magnitude when the doping ratio is 0.10%. This phenomenon can be interpreted that the substitution of Ag<sup>+</sup> at Ba<sup>2+</sup> site is linked to the creation of oxygen vacancies for charge compensation which serves as the positive center for transmission. However, the increment of oxygen vacancies caused by the further doping promotes the distortion of crystal lattices, which enhances the resistivity even beyond 2.00×10<sup>7</sup> Ω·m. Simultaneously, gaseous penetration of La also can promote the electrical conductivity, while this effect is corresponded with the doping of Ag<sup>+</sup>. It is believed that the acceptor dopant is tended to exist at grain boundary regions, which forms the depletion layer that blocks the La<sup>3+</sup> penetrated into the bulk regions at low doping ratio. And this penetration is regarded to be the key step of the promotion to the conductivity. Hence, as notified in the table, the resistivity of the LBATO with doping ratio is 0.05% is increased, which is different from all the others. Yet, when the concentration of acceptor dopant is beyond 0.01%, the distortion of crystal lattices is aggravated so as to weaken the depletion layer, which is helpful to the penetration of La<sup>3+</sup>. These two effects act together to generated the lowest point 2.45×10<sup>5</sup> Ω·m of BLATO.

### 2.2 XRD analysis of La penetrated BATO powders

The XRD patterns of BTO, BATO, and LBATO are illustrated in Fig. 1. And the blank experiment of penetration is shown in Fig. 2.

To understand the changes in structure and constitution, comparison of XRD patterns is illustrated in Fig. 1, which indicates that the doping process did not change the perovskite structure and the main phases of the nanocrystalline powders. While the penetration process of La<sup>3+</sup> leads to the change in constitution. Characteristic peaks of new phase,

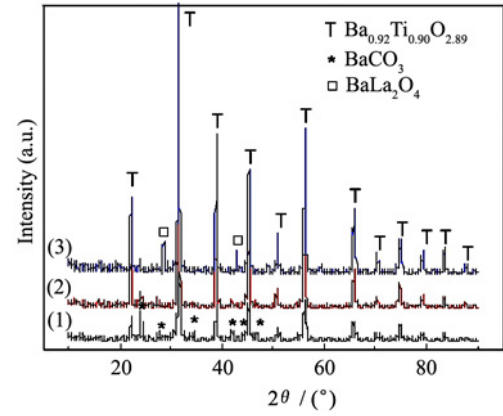


Fig. 1 Comparison of XRD patterns

(1) BTO; (2) BATO; (3) LBATO

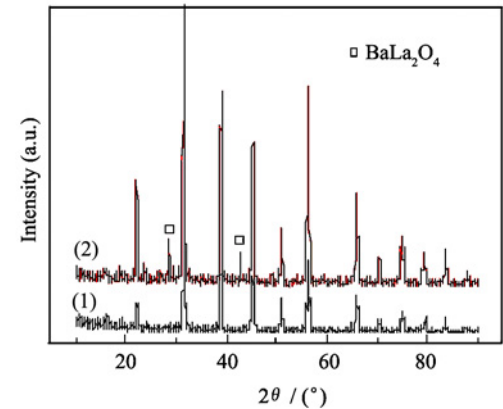


Fig. 2 XRD patterns of blank experiment

(1) Penetrated without La; (2) Penetrated with La

BaLa<sub>2</sub>O<sub>4</sub> (ICCD 42-1500), appears at 28.5° and 42.8° after penetration process, which is believed as the key factor for promoting the electrical conductivity significantly. Based on the blank assay which is penetrated without La<sup>3+</sup>, we speculate that the reaction related to La<sup>3+</sup> took place during the penetration process as the follow equation:



It is concluded from Eq. (1) that La<sup>3+</sup> penetrated into the crystal lattices in the form of substituting the Ti<sup>4+</sup> site.

### 2.3 SEM photos and EDAX of La penetrated BATO powders

The morphology of the samples was detected by SEM which is illustrated in Fig. 3.

From the comparison of SEM photos before and after penetration without La<sup>3+</sup>, it can be concluded that penetration process, itself, promotes the partly sintering of the powders which benefits the generation of the electrically conductive paths. Furthermore, the intervention of La<sup>3+</sup> in the gaseous penetration process stimulates the partly sintering even better, which is illustrated in SEM photo (c). It is believed that the sintering of powder benefits the conductivity physically, while the penetration with La<sup>3+</sup> changed both the morphology and constitution in the form of generating new compounds which promoted the conductivity significantly. And the analysis above is corresponded with the conclusion of XRD.

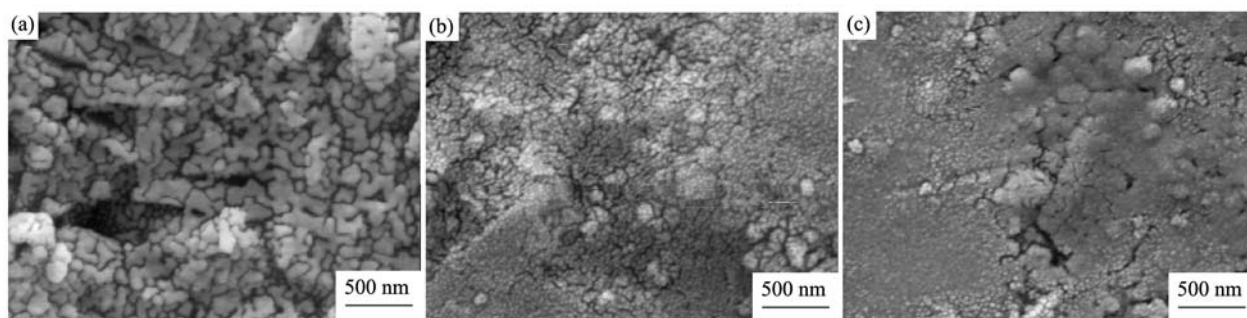


Fig. 3 SEM photos of gaseous penetration modified BT powders  
(a) Before penetrated; (b) After penetrated without  $\text{La}^{3+}$ ; (c) After penetrated with  $\text{La}^{3+}$

**Table 2 Results of EDAX analysis of LBATO powders**

Elements	C	O	Ba	Ti	Ag	La
Concentration/at. %	29.95	19.51	39.05	9.68	0.73	1.08

To support the conclusion of SEM, EDAX of the sample after penetration with  $\text{La}^{3+}$  is detected, and the result is listed in Table 2.

The data from the table provide the relative concentration of main elements in the sample. Definitely, the element La does exist, which is linked to the penetration process. Moreover, coupled with the results of XRD, we infer that the sintering phenomenon partly results from the new rare earth compound ( $\text{BaLa}_2\text{O}_4$ ) which is generated by the complex reaction during the penetration process. The concentration ratio of Ba, Ti, and O tends to be 4:1:2. Based on the analysis above, it is known that the elements of Ti and O are lost in the forms of  $\text{TiO}_2$  during the penetration process, which is another evidence of Eq. (1) we speculated before.

#### 2.4 FTIR analysis of La penetrated BATO powders

Further structural detection of the LBATO powders has been done by FTIR, which is depicted in Fig. 4.

The characteristic absorption around  $3400\text{ cm}^{-1}$  is assigned to  $-\text{OH}$  stretching vibration, due to the  $\text{H}_2\text{O}$  brought by KBr or absorbed on the powder surface during the pre-process. In agreement with the XRD analysis, the characteristic absorption around  $1440\text{ cm}^{-1}$  is assigned to the

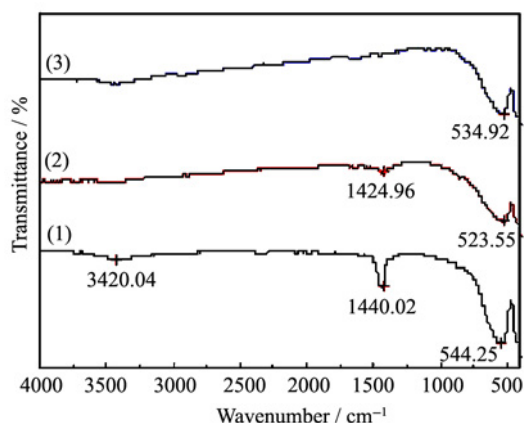


Fig. 4 FTIR spectra of the samples  
(1) BTO; (2) BATO; (3) LBATO

stretching vibrations of carboxylate, which indicates the presence of  $\text{BaCO}_3$  in the samples before penetration of  $\text{La}^{3+}$ . All the three samples display strong absorptions  $550\text{ cm}^{-1}$  to  $520\text{ cm}^{-1}$ , which can be assigned to the stretching and bending vibrations of the  $\text{Ti-O}$  bond in  $[\text{TiO}_6]^{2-}$  octahedron in  $\text{BaTiO}_3$  crystal. However, variation in the strongest absorption can be detected, which indicates that penetration of  $\text{La}^{3+}$  restrains the blue shift caused by doping. It is concluded that the substitution of  $\text{La}^{3+}$  at Ti site strengthens the  $\text{Ti-O}$  bond via the gaseous penetration process.

### 3 Conclusions

The acceptor dopant Ag owned the ability to decrease the resistivity of the BTO-based powders, yet, the gaseous penetration of La successively reduced the resistivity of BATO to the lowest point of  $2.45 \times 10^5\text{ }\Omega\cdot\text{m}$ .

XRD analysis indicated that  $\text{La}^{3+}$  penetrated into the crystal lattices in the form of substituting the  $\text{Ti}^{4+}$  site. And this substitution strengthened the  $\text{Ti-O}$  bond which led to the inhibition of blue shift caused by doping detected by FTIR.

The analysis of morphology illustrated that the penetration process promoted the partly sintering of BATO powders and the intervention of  $\text{La}^{3+}$  aggravated this effect.

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