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Studies on the preparation of positive, temperature coefficient of resistivity powder by two chemical steps

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Ultrafine and homogeneous positive temperature coefficient of resistivity (PTCR) powder was prepared by two chemical steps: citrate and liquid-phase coating process. The physical and chemical properties of the powder were investigated in detail. The dimensions of the primary particles in the PTCR powders were about 20–50 nm. Sintering aids and acceptors could be distributed homogeneously in doped $BaTiO_3$ powder through the liquid-phase coating process. Sintered from this powder produced samples with excellent PTCR effects ($\Delta R = 10^6$, $\Delta T = 110\,^\circ C$, $\alpha_{30} = 26\%\,^\circ C^{-1}$).

1. Introduction

Positive temperature coefficient of resistivity (PTCR) ceramic is a typical kind of multicomponent functional ceramic. It is based on semiconducting $BaTiO_3$ ceramics, and Ba^{2+} is usually substituted partially by Ca^{2+}, Sr^{2+} and Pb^{2+} to suit different requirements. To improve the PTCR performance sharply, sintering aids (such as Al_2O_3, SiO_2, Li_2O, etc.) and acceptors (such as MnO) are also necessary.

The PTCR performance is an effect of the grain boundary [1]. The main compositions of a grain boundary are sintering aids and acceptors. Sintering aids not only restrain the grain's abnormal growth, they can also absorb acceptors. Acceptors play an important role in the PTCR performance when they are well distributed in a grain boundary [2]. To ensure sintering aids and acceptors are distributed in the grain boundary, conventionally PTCR powders are prepared in two steps [3]: firstly, the doped $BaTiO_3$ powder is synthesized by the solid-state reaction which requires a grinding process; secondly, the presynthesized powder, sintering aids and acceptors, are ground together again. This method requires two grinding processes: in the second grinding process, the presynthesized powder is too hard to be crushed easily. So the homogeneity of the sintering aids and acceptors is poor. Ravi and Kutty [4] have reported a novel method for the incorporation of sintering aids and acceptors in PTCR ceramic. They dipped the presintered porous disc of doped $BaTiO_3$ in aqueous solutions containing sintering aids and acceptors. Although this method can ensure that sintering aids and acceptors are distributed in the grain boundary, the porosities of the disc are irregular, and the homogeneity of sintering aids and acceptors is also poor. Because of the special demands (some compositions must be distributed in the grain boundary) of PTCR, it is difficult to prepare PTCR powder by the average chemical method in one step. In this paper, we report a new method for preparing PTCR powder via two chemical steps. Firstly, the ultrafine doped $BaTiO_3$ powder is synthesized by the citrate process [5, 6] at low temperature; secondly, sintering aids and acceptors are incorporated by a liquid-phase coating process [7].

2. Experimental procedure

In this experiment, we choose Ca^{2+} and Sr^{2+} to substitute Ba^{2+}, Y^{3+} as doping elements, SiO_2 and Al_2O_3 as sintering aids, and MnO as the acceptor.

2.1. Preparation of doped $BaTiO_3$ powder

Fig. 1 illustrates the experimental procedure for preparing the ultrafine doped $BaTiO_3$ powder. The starting materials were barium citrate [$Ba(C_6H_6O_7)$],

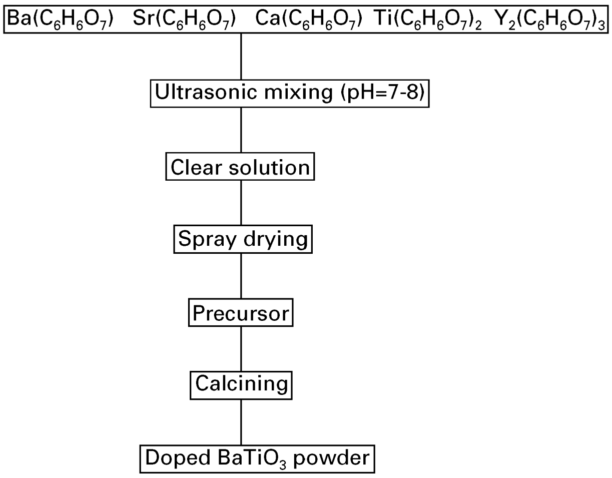

Figure 1 Flow chart showing the preparation procedure for doped $BaTiO_3$ powder.

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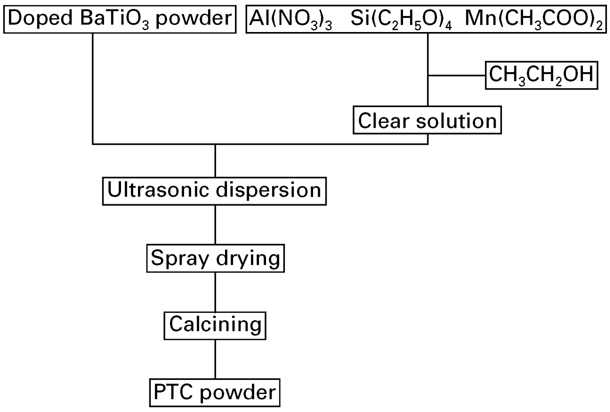


Figure 2 Flow chart showing the incorporation procedures of sintering aids and acceptor.

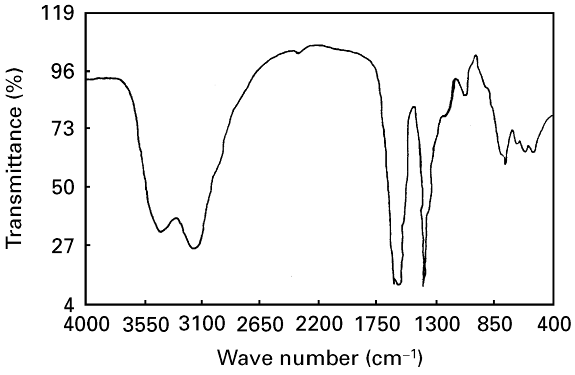


Figure 3 Infrared spectrum of the mixed citrate solution.

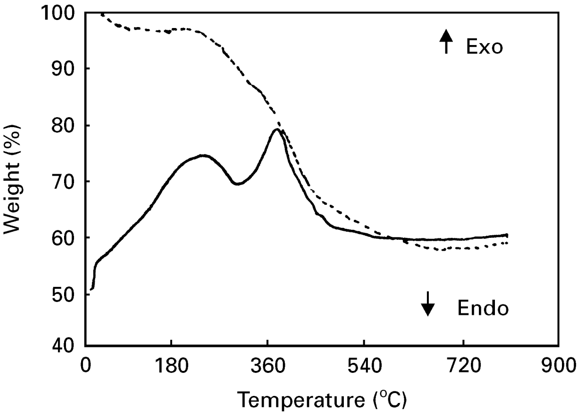


Figure 4 (—) Differential and (– – –) thermogravimetric analysis of the citrate precursor.

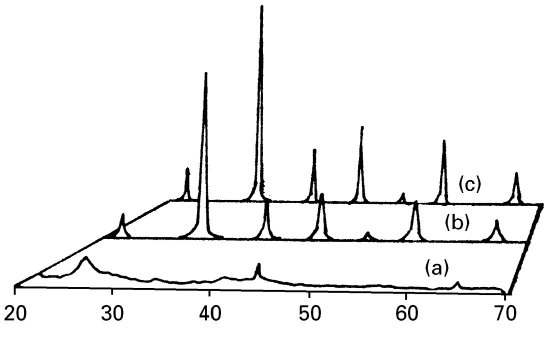


Figure 5 X-ray diffraction for the product calcined at (a) 450 °C, (b) 500 °C, (c) 600 °C.

strontium citrate [Sr($C_6H_6O_7$)], calcium citrate [Ca($C_6H_6O_7$)], titanium citrate [Ti($C_6H_6O_7$)$_2$] and yttrium citrate [Y_2($C_6H_6O_7$)$_3$]. These citrate solutions were prepared according to procedures reported previously by the authors [8]. When five solutions were mixed together, the pH value was adjusted to 7–8 through the addition of liquid ammonia, and under ultrasonic mixing conditions, clear solutions of five compositions could be obtained. After being spray dried, the solution transformed into an amorphous precursor. The precursor was calcined at 450°, 500 and 600 °C, respectively.

The structure of the solution containing five compositions was examined by infrared spectrometry, using KBr as the medium. Thermogravimetric (TGA)

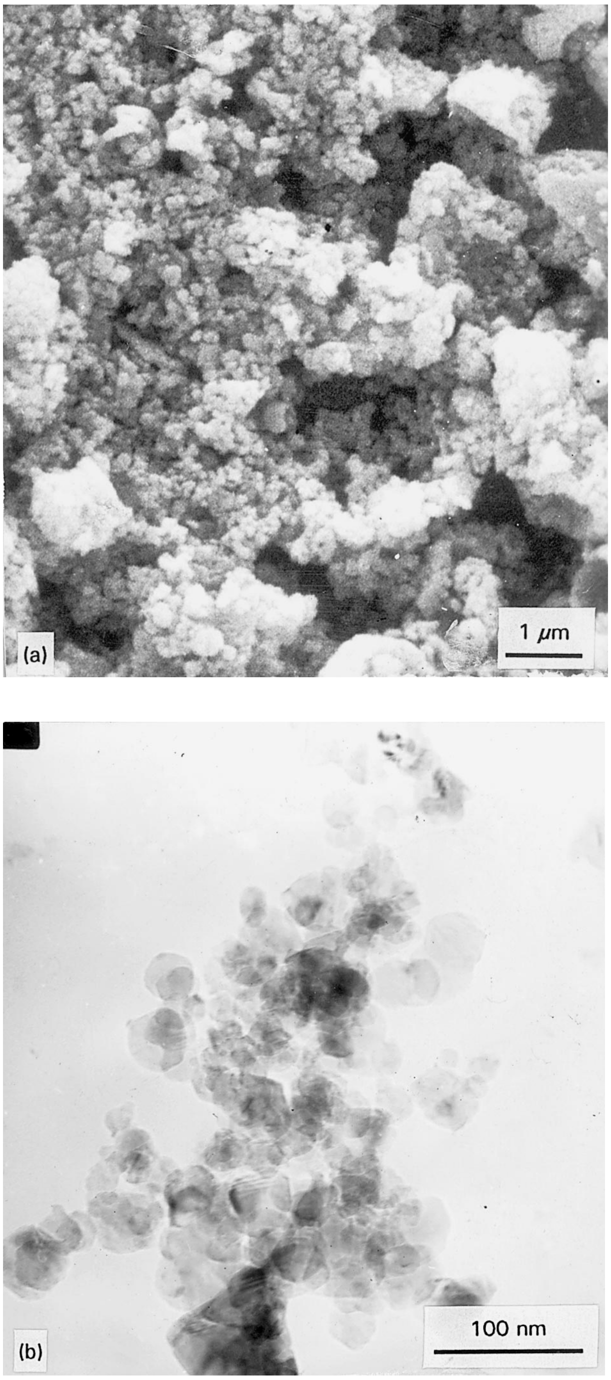


Figure 6 Electron micrographs of doped $BaTiO_3$ powder after calcining at 600 °C for 2 h. (a) Scanning electron micrograph, (b) transmission electron micrograph.

and differential thermal analysis (DTA) studies were carried out at a heating rate of 10 °C min^{-1}. The development of a crystalline doped $BaTiO_3$ phase was monitored using X-ray powder diffraction. The particle size and shape of the powder were assessed by scanning and transmission electron microscopies.

2.2. Incorporation of sintering aids and acceptor

Fig. 2 illustrates the coating procedure for incorporating sintering aids and acceptor. The starting materials were doped $BaTiO_3$ powder from above, $Al(NO_3)_3$, $Si(C_2H_5O)_4$ and $Mn(CH_3COO)_2$. The solution containing three compositions was prepared as follows: $Al(NO_3)_3$ and $Mn(CH_3COO)_2$ were dissolved in distilled water, $Si(C_2H_5O)_4$ was dissolved in ethanol. After the three solutions were mixed together, ethanol was added continuously until the solution became clear. When dispersing the doped $BaTiO_3$ powder into the solution of three compositions, ultrasonic dispersion was necessary to induce the powder to suspend in the solution homogeneously. After being spray dried, the coated powder was calcined at 600 °C for 1 h to remove the remaining organics. To detect the homogeneity of Al_2O_3, SiO_2 and MnO, inductively coupled plasma (ICP) analysis was utilized according to procedures reported previously by the authors [9].

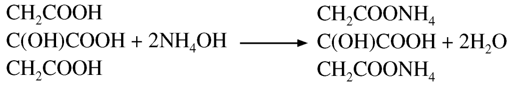
2.3. Samples and measurement

The PTCR powder, which was obtained from the above procedure, was mixed with binder (8 wt %) homogeneously and pressed at 1000 p.s.i., (10^3 p.s.i. = 6.89 N mm^{-2}) then sintered. The natural surface and morphology of a grain boundary of an as-fired sample were examined by SEM. The examinations of sintered samples involving electrical properties were measured by IEC standards.

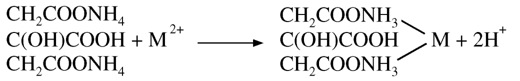
3. Results and discussion

3.1. Doped $BaTiO_3$ powder

Citric acid is a useful complex which can react with many metal ions under ammonia, conditions such as Ba^{2+}, Ca^{2+}, Zr^{4+}, Mg^{2+}, Ti^{4+}, etc. Therefore, it could be used to prepare the multicomponent solution. In this experiment, the key chemical reactions between metal ions and citric acid were as follows:

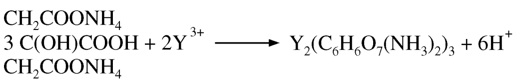


$$\begin{array}{l}\mathrm{CH_2COOH}\\ \mathrm{C(OH)COOH + 2NH_4OH}\\ \mathrm{CH_2COOH}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2COONH_4}\\ \mathrm{C(OH)COOH + 2H_2O}\\ \mathrm{CH_2COONH_4}\end{array} \quad (1)$$

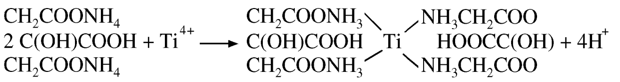


$$\begin{array}{l}\mathrm{CH_2COONH_4}\\ \mathrm{C(OH)COOH + M^{2+}}\\ \mathrm{CH_2COONH_4}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2COONH_3}\diagdown\\ \mathrm{C(OH)COOH} > \mathrm{M + 2H^+}\\ \mathrm{CH_2COONH_3}\diagup\end{array} \quad (2)$$

(M = Ba, Ca, or Sr)



$$\begin{array}{l}\mathrm{CH_2COONH_4}\\ \mathrm{3\,C(OH)COOH + 2Y^{3+}}\\ \mathrm{CH_2COONH_4}\end{array} \longrightarrow \mathrm{Y_2(C_6H_6O_7(NH_3)_2)_3 + 6H^+} \quad (3)$$



$$\begin{array}{l}\mathrm{CH_2COONH_4}\\ \mathrm{2\,C(OH)COOH + Ti^{4+}}\\ \mathrm{CH_2COONH_4}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2COONH_3}\diagdown\\ \mathrm{C(OH)COOH}\ \mathrm{Ti}\\ \mathrm{CH_2COONH_3}\diagup\end{array} \begin{array}{l}\diagup\mathrm{NH_3CH_2COO}\\ \mathrm{HOOCC(OH) + 4H^+}\\ \diagdown\mathrm{NH_3CH_2COO}\end{array} \quad (4)$$

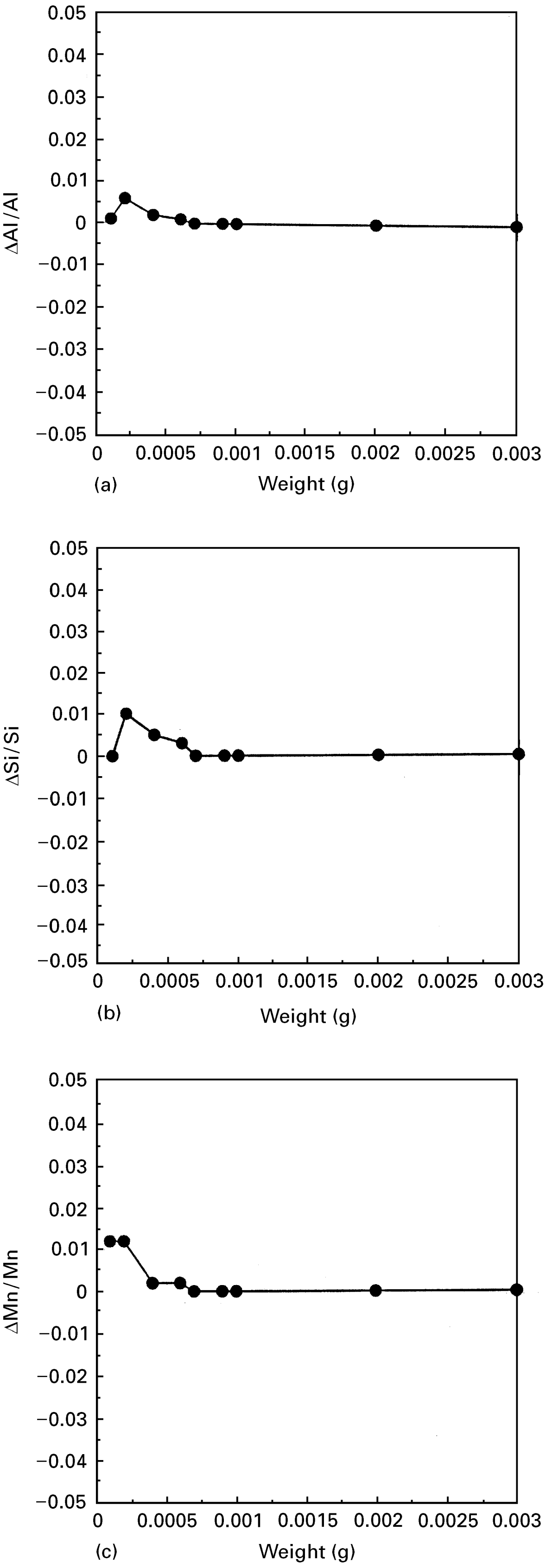


Figure 7 ICP analysis results on the chemical homogeneity of (a) Al_2O_3, (b) SiO_2 and (c) MnO.

The infrared pattern (Fig. 3) of mixed citrate solution is shown to confirm the formation of a citrate complex compound.

Differential and thermogravimetric analyses of the precursor formed by spray drying the mixed citrate solution are shown in Fig. 4. The final weight loss in the TGA experiments occurred at about 550 °C, indicating that the DTA exotherms occurring below this temperature were associated with organic decomposition processes.

Fig. 5 shows the XRD pattern of the products at different temperatures. The results demonstrated that amorphous precursors gradually transformed to the crystalline phase from 450–500 °C, but the peak intensity was low at 500 °C. At 600 °C, the peaks were sharp. This indicated that the amorphous precursor had been crystallized perfectly at this temperature. This result was also in agreement with the above results of TGA and DTA.

The morphologies of powders formed by calcining the precursor at 600 °C for 2 h are shown in Fig. 6. The SEM (Fig. 6A) provided a visual way of observing the powders, which consisted of agglomerates of round particles. These agglomerates were porous and easily breakable owing to the larger molecular structure of citrate and the evaporation of H_2O, CO and CO_2 produced during the process of calcination. Transmission electron microscopy identified primary particles that were only 20–50 nm in size within the agglomerate (Fig. 6B).

3.2. Homogeneity of Al_2O_3, SiO_2 and MnO

The doped $BaTiO_3$ powder was prepared from the clear solution through the spray drying and calcining process, so the homogeneity of Ba^{2+}, Ca^{2+}, Sr^{2+}, Y^{3+} and Ti^{4+} remained molecular in size. Al_2O_3, SiO_2 and MnO were incorporated by the liquid-phase coating process, so it was necessary to detect the homogeneity of these three compositions in the PTCR powder. We utilized ICP analysis to monitor the homogeneity. ICP analysis demanded a decreasing weighing process. At each weighing, it should analyse the extent of the deviation of the compositions from the idea ratio. The weight at which the deviation was at a constant level was a standard of the homogeneity. The less the amount of powder weighed, the better was the homogeneity. Fig. 7 illustrates the homogeneity of Al_2O_3, SiO_2 and MnO. We found that their homogeneities were very good. At 0.00075 g, the deviation from the ideal ratio of these three compositions became zero.

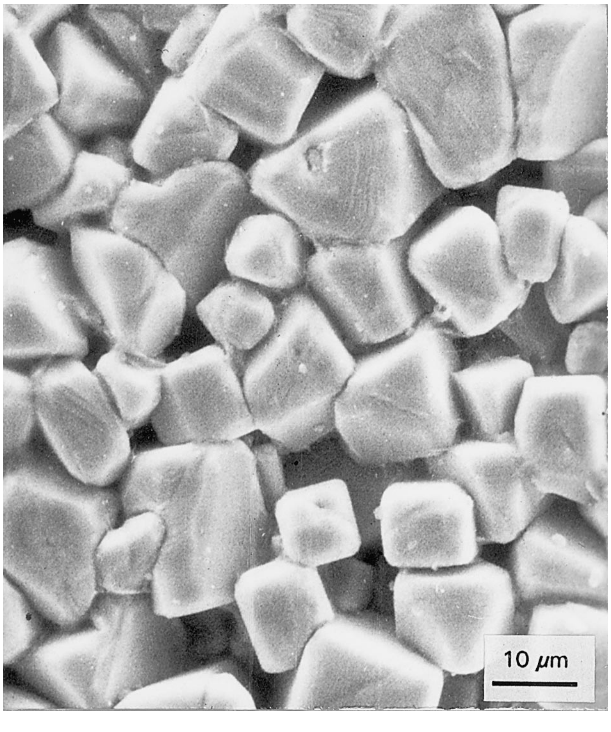


Figure 8 Scanning electron micrograph of the natural surface of the as-fired sample.

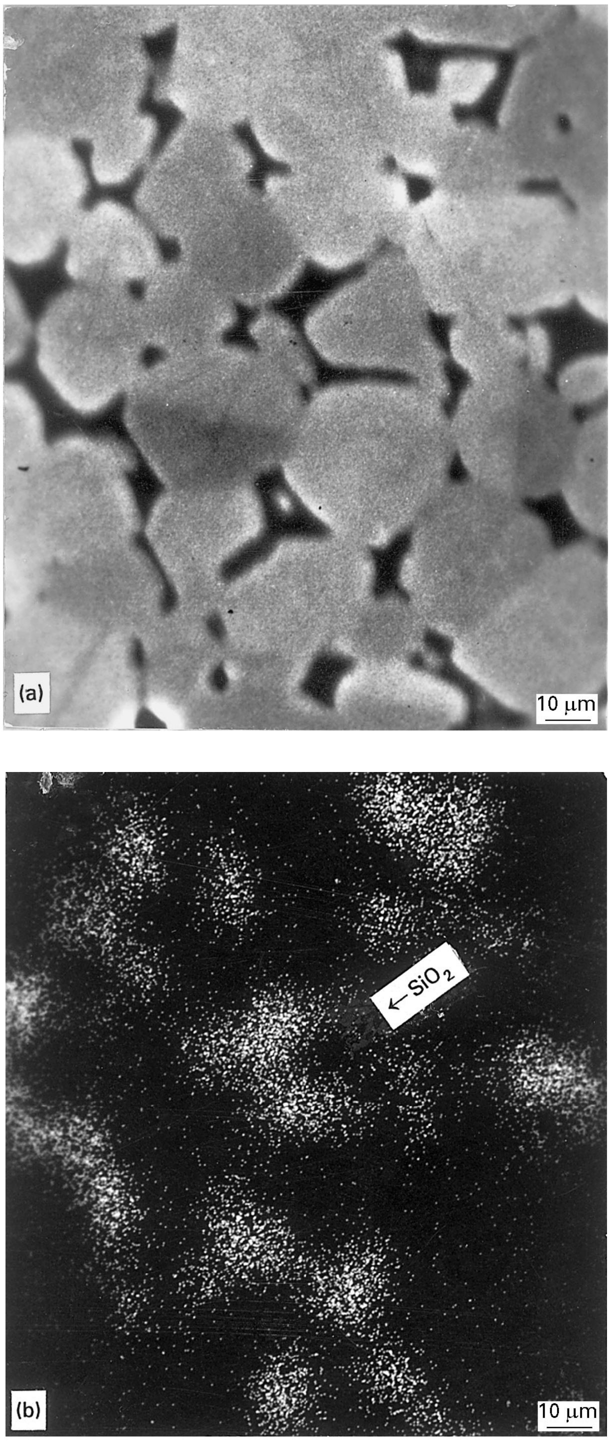


Figure 9 Scanning electron micrographs of the distribution of SiO_2 in the grain boundary.

3.3. Sintering and electrical properties

The natural surface of the as-fired sample, as examined with the SEM, is shown in Fig. 8. It was found

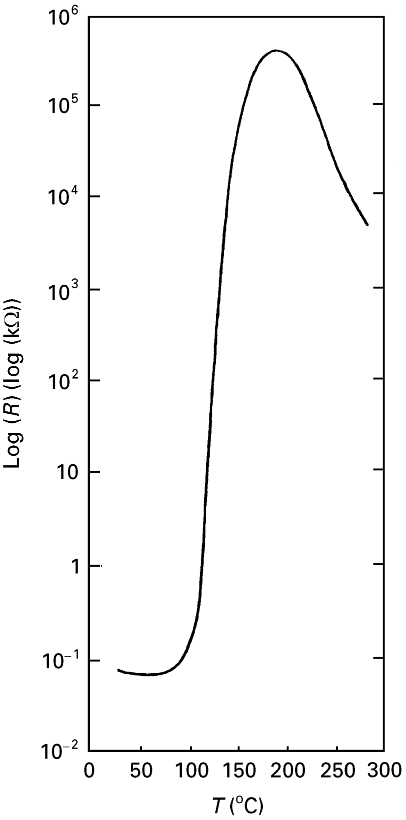


Figure 10 R–T curve of the as-fired sample.

that the grains of sample grew completely and evenly, the average size of grains being about 5–10 µm. This resulted from the good homogeneity of Al_2O_3 and SiO_2. Fig. 9 shows the distribution of SiO_2 (amounts of Al_2O_3 and MnO were too small to be detected with SEM). Comparing Fig. 9a and b, we see that SiO_2 was well distributed in the grain boundary, but was hardly detected in the grain bulk. This confirmed that the distribution of sintering aids was controlled in the grain boundary by the liquid-phase coating process.

The PTCR effects of the as-fired sample are shown in Fig. 10. The jump in the resistivity was about 10^6, $\Delta T(R_{\min}$ to $R_{\max})$ was about 110 °C, the temperature coefficient of resistivity, α_{30}, was 26% $°C^{-1}$. α_{30} was counted according to the following equilibrium

$$\alpha_{30} = \ln(R_{T_c+30}/R_{T_c})/30 \qquad (5)$$

The relation between microstructure and electrical properties of the as-fired sample in this experiment will be discussed in detail in another paper here. Only the major electrical properties of the as-fired sample are given here.

4. Conclusion

It has been demonstrated that a stable solution containing Ba^{2+}, Ca^{2+}, Sr^{2+}, Ti^{4+} and Y^{3+} could be prepared via the citrate process. By spray drying and calcining, ultrafine and homogeneous PTCR barium titanate powder could be obtained via the liquid-phase coating process, Al_2O_3, SiO_2 and MnO could be well distributed in the grain boundary. The excellent PTC effects could be obtained by sintering this powder. This method is suitable for preparing all kinds of functional ceramic powders.

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