New route for preparing $BaTiO_3$ nanometer powders

YONG ZHANG
College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, People's Republic of China; School of Materials Science and Engineering, Wuhan Institute of Chemical Technology, Wuhan 430073, People's Republic of China

SHITING LUO, YANG FU
College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, People's Republic of China

KELI ZHANG*
College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, People's Republic of China; Center of Nanoscience and Nanotechnology Research, Wuhan University, Wuhan 430072, People's Republic of China
E-mail: klzhang@whu.edu.cn

In view of achieving better control over physical and chemical characteristics, there is considerable interest in evaluating new methods for the synthesis of $BaTiO_3$ (BT) powders, and a great effort has been devoted to the development of new methods [1–6]. In this work, a rheological phase reaction method was introduced to synthesize BT nanometer powders of which structure was studied at room temperature. Rheological phase reaction method is a process of preparing compounds or materials from solid–liquid rheological mixture. That is, the solid reactants were fully mixed in a proper molar ratio, made up by adding a proper amount of water or other solvents to a solid–liquid rheological body in which the solid particles and liquid substance were uniformly distributed. Then after reaction under suitable conditions, the product was obtained. Under the solid-liquid rheological state, many substances have new reaction properties. Comparing with other methods, the one mentioned in this paper has two merits; first, the whole process is simple, soft, and green, and second, the Ba/Ti ratio was easily controlled at 1:1.

The BT nanometer powders were prepared by thermal decomposition of its peroxide precursor. In order to prepare peroxide precursor, commercially available $Ba(OH)_2{\cdot}8H_2O$ (AR, purity >99%), $H_2TiO_3{\cdot}5H_2O$ (AR), H_2O_2 solution (AR, >30%), and $CO(NH_2)_2$ (AR, purity >99%) were used as starting materials. Firstly, $Ba(OH)_2{\cdot}8H_2O$ (0.01 mole) and $H_2TiO_3{\cdot}5H_2O$ were mechanically milled homogeneously in Ba/Ti molar ratio of 1.01:1, and then the H_2O_2 solution with $CO(NH_2)_2$ dissolved into it was added in amounts of 2.5 times in molar of $Ba(OH)_2{\cdot}8H_2O$. The mixture soon became solid-liquid rheological state by slightly milling. As a result, the peroxide precursor was obtained after 10 min at room temperature [7]. In this experiment, first, H_2O_2 is used to dissolve H_2TiO_3 and second, the gas released by the decomposition of H_2O_2 could make fine the grain size of the peroxide precipitation. For $CO(NH_2)_2$, the main role first is used to improve the chemical stability of H_2O_2 and delay the decomposed rate of H_2O_2; second, solid state $CO(NH_2)_2$ could adjust the whole reaction system to become rheological phase state; and third, the decomposition of $CO(NH_2)_2$ could make more fine the grain size of $BaTiO_3$. The formation mechanism of peroxide precursor can be illustrated by the following equations:

$$H_2TiO_3 + H_2O_2 \rightarrow TiO_4^{2-} + 2H^+ + H_2O$$

$$Ba(OH)_2 + TiO_4^{2-} + 2H^+ \rightarrow BaTiO_4 \downarrow + 2H_2O$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$$

The peroxide precursor was washed by nonironic or iron–free water and then by anhydrous ethanol and kept for TG and IR analysis. According to the TG and DTA data, the precursor was divided into four groups which were treated under following conditions: below 120 °C for 3 hr, at 500 °C for 3 hr, at 600 °C for 0 min, and at 700 °C for 10 min.

The TG and DTA curves of the precursor were obtained by using SHIMADZU DT-40 at atmospheric air with a steady calefactive rate of 20 °C/min. The XRD plots were collected by using X-rays diffraction (XRD-6000) with $CuK\alpha_1$ radiation at room temperature. The TEM photo was gained by using the instrument of TEM-100CX at 80 kv, and the DSC curve was obtained by using Netzsch DSC200PC instrument.

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* Author to whom all correspondence should be addressed.

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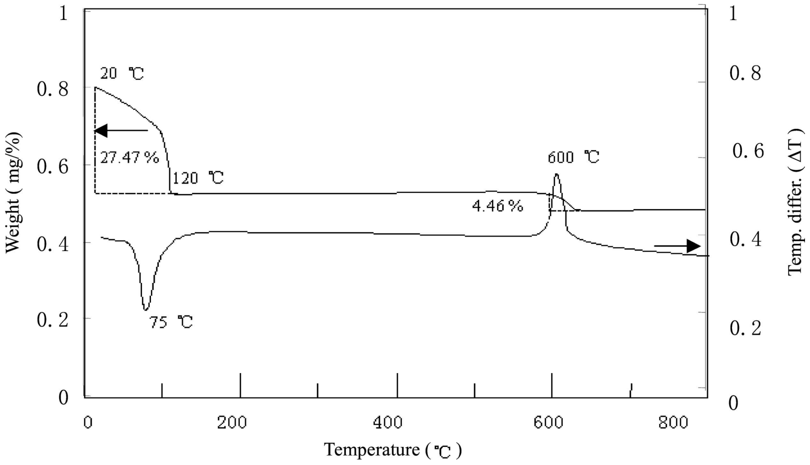

Figure 1 TG and DTA curves of precursor.

Fig. 1 is the TG and DTA curves of precursor, and two decomposition steps were distinctly displayed. In the DTA curve, it could be concluded that the crystal water was lost in the first step by the fact that the first decomposition step was endothermic below 120 °C.

Fig. 2 is the IR Spectra of thermal decomposition products. The spectrum of product below 120 °C presented the peroxide bond vibrations of 1362.6 and 890.5 cm^{-1}. In the spectrum of product at 500 °C, the peak of 890.5 cm^{-1} was concealed by other wider peaks, the peak of 1362.6 cm^{-1} displaced to 1384.4 cm^{-1}, and no OH group vibrations were observed. In the spectrum of 600 and 700 °C, no peroxide bond or OH group vibrations were observed. It proved that transitional product may be peroxide and that it decomposed into oxides at 600 °C. It was also confirmed by DTA curve that the second step was exothermic.

The chemical formula of the precursor was calculated as $BaTiO_4{\cdot}5H_2O$, and the calculated data were listed in Table I.

The thermal decomposition mechanism of the peroxide precursor was determined as follows:

$$BaTiO_4{\cdot}5H_2O \rightarrow BaTiO_4 + 5H_2O$$

$$BaTiO_4 \rightarrow BaTiO_3 + 0.5O_2$$

The XRD plots of all the products were listed in Fig. 3, and the formation of the BT powders was distinctly

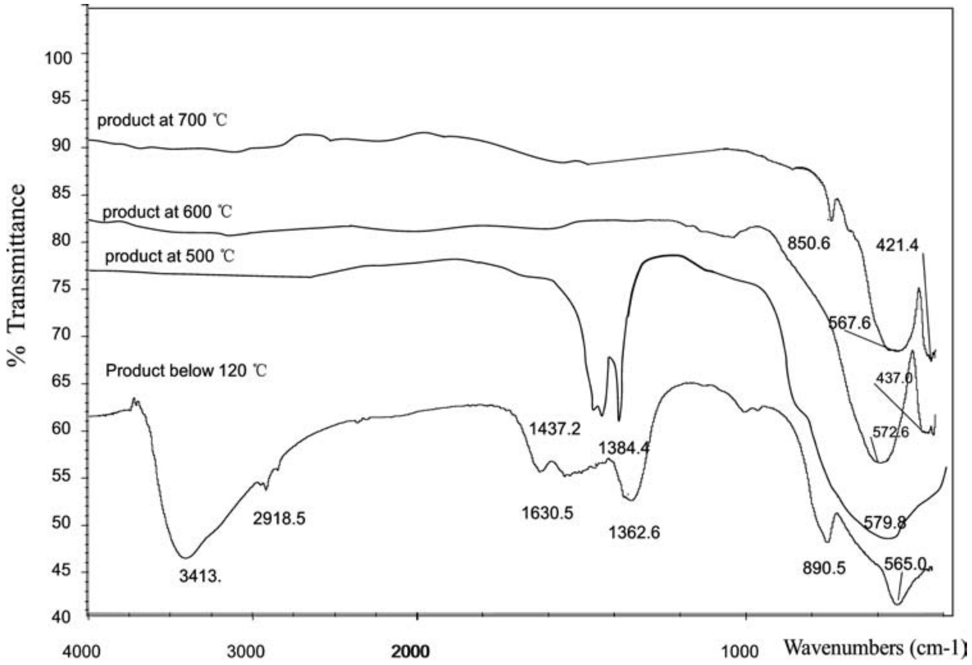

Figure 2 IR Spectra of thermal decomposition products.

TABLE I The TG data of the precursor

	1st step (%)	2nd step (%)
Exp. data	27.47	4.46
Calc. data	26.25	4.67

revealed. According to the thermal decomposition mechanism of the peroxide precursor, curves 1 and 2 were considered as the XRD plots of $BaTiO_4$ which indicated that the $BaTiO_4$ was amorphous because no obvious peaks were observed. When the temperature was raised to 600 °C, the BT phase appeared at this turning point which was shown by curve 3, and the BT phase would be formed completely, if kept the precursor was kept at 600 °C for 10 min. Curve 4 was the XRD plot of BT powders.

Fig. 4 was the TEM photo of the BT powders, and it indicated that the distribution of the particle size was not homogeneous. In fact, the particle sizes of the great mass of the BT powders were below 20 nm while some of them were more than 30 nm, and the average particle size was 22.5 nm.

It was well known that the Curie point decreases with decreasing particle sizes in ferroelectric fine particles, and that the ferroelectric fine particle with different particle size has different Curie point [8–11]. In the ideal BT crystal, the Curie point is around 120 °C and no phase transition happens between 0 and 120 °C. In the DSC experiment, no peak was found around 120 °C. The DSC plots of BT powders as prepared between −150 and 200 °C were shown in Fig. 5. The observed peaks at 8.0 and 20.1 °C were the curie points of the BT powders,

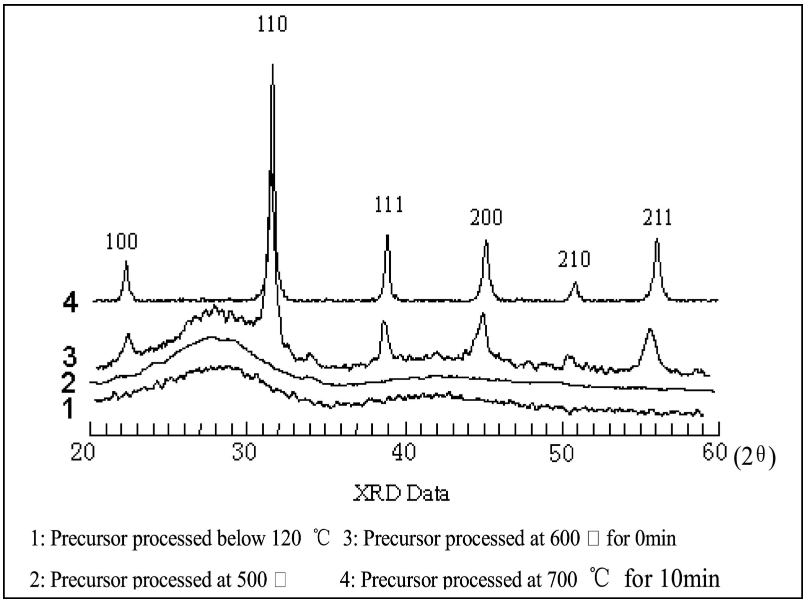

Figure 3 The XRD plots of specimens.

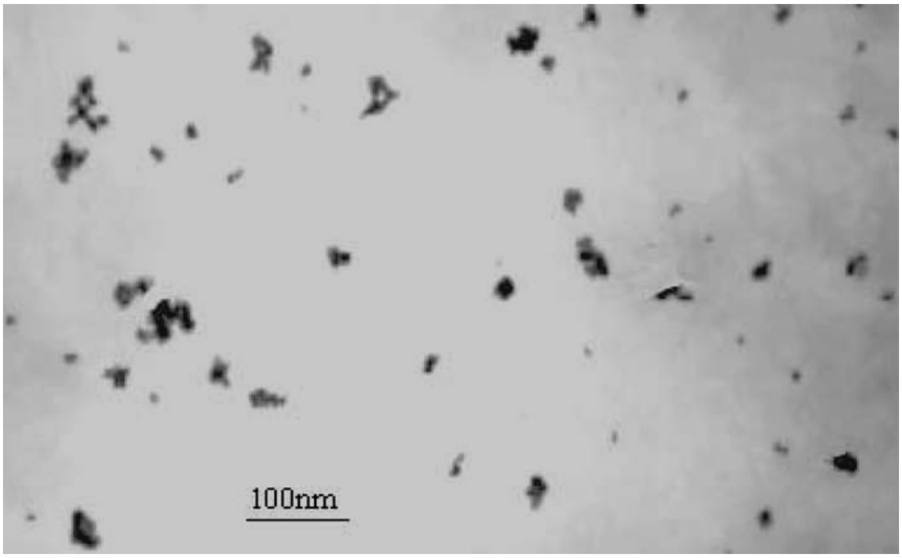

Figure 4 The TEM photos of BT powders.

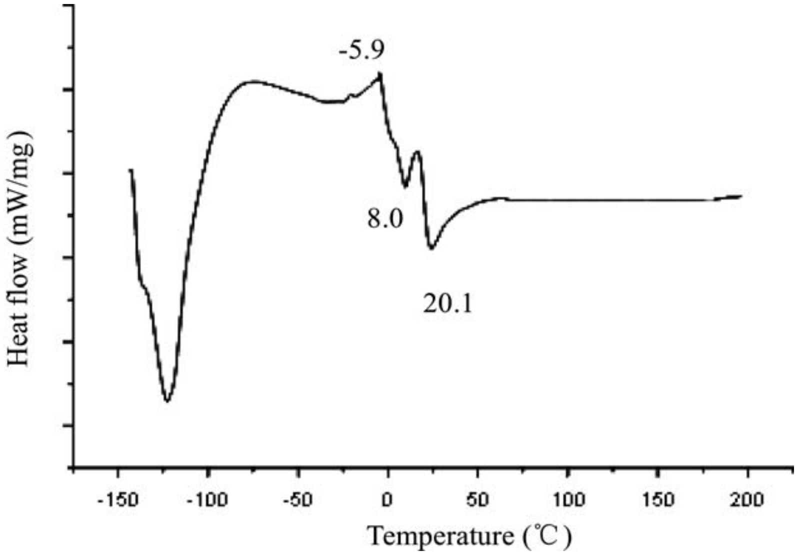

Figure 5 The DSC plots of BT powders.

which indicated that the phase of the BT powders as prepared was cubic at room temperature and that their particles were of various size [8–11].

Acknowledgments

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