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Thermal analysis of formation of nano-crystalline $BaTiO_3$ using $Ba(NO_3)_2$ and TiO_2

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Abstract

The reaction of $Ba(NO_3)_2$ with TiO_2 was studied by thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques up to 1000 °C and in nitrogen atmosphere. It was found that the formation of $BaTiO_3$ takes place above 600 °C and that precursor mixing time and heating rate have no effect on the reaction temperature. $BaTiO_3$ powder was prepared by calcination of $Ba(NO_3)_2$ and TiO_2 precursor mixture at 800 °C for 8 h. X-ray diffraction analysis of the synthesized $BaTiO_3$ confirmed the formation of tetragonal phase with lattice parameters a = 3.9950±0.0003 Å and c = 4.0318±0.0004 Å. Thermal analysis of the synthesized $BaTiO_3$ powder showed weight loss within temperature range 40–1000 °C of only 0.40%. This small amount of weight loss was connected with some impurity phase, and identified as $BaCO_3$ using Fourier transform infrared (FTIR) technique.

Keywords: *synthesis, barium titanate, $Ba(NO_3)_2$ precursor, thermal analysis, XRD, FTIR*

I. Introduction

Performance of $BaTiO_3$ ceramics significantly depends on the microstructure of the sintered body, which is influenced by characteristics of the starting $BaTiO_3$ powder. Therefore, much attention has been focused on the synthesis of high quality $BaTiO_3$ nano-particles and different techniques have been used: sonochemical synthesis [1], sol-gel [2], hydrothermal [3], solvothermal [4], chemical co-precipitation [5] and supercritical fluid [6]. These methods are not cost-effective in mass production of $BaTiO_3$ nanopowders. Thus, preparation of $BaTiO_3$ powders, using solid state reaction synthesis is regarded as one of the most practical and economical ways [7]. However, in the conventional solid phase methods, $BaTiO_3$ powders were usually produced via the reaction between the mechanically mixed $BaCO_3$ or BaO and TiO_2 powders followed by calcination at above 1000 °C [8]. Unfortunately, the reactions at such high temperatures are beyond control and the resultant powders often have large particle size and wide particle size distribution. Therefore, for industrial applications, it is still desirable to develop an alternative low-temperature solid state method for the preparation of nano-crystalline $BaTiO_3$ powders at low cost.

Researchers have tried to synthesize $BaTiO_3$ powders at lower temperatures by replacing $BaCO_3$ by other compounds such as $Ba(OH)_2$, $Ba(COO_2)$, $Ba(NO_3)_2$ etc. [9]. Thus, it was reported that the reaction of $Ba(NO_3)_2$ with TiO_2 (anatase) yielded the single phase $BaTiO_3$ at much lower temperatures, around 600 °C [10–12], but this method has not been studied in details like a synthesis of $BaTiO_3$ using $BaCO_3$ and TiO_2. Therefore, the aim of this work is to study the formation of $BaTiO_3$ from $Ba(NO_3)_2$ and TiO_2, using thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis. Further characterization of the prepared $BaTiO_3$ powder was done using thermal analysis (TG and DSC), X-ray diffraction (XRD) and Fourier Transform Infra-red (FTIR) techniques.

II. Experimental

2.1. Sample preparation

$BaTiO_3$ powder was prepared by using $Ba(NO_3)_2$ (purity 99%, Qualikens, USA) and titanium dioxide (rutile TiO_2 purity 99.5%, Alfa Aesar, UK) as the starting

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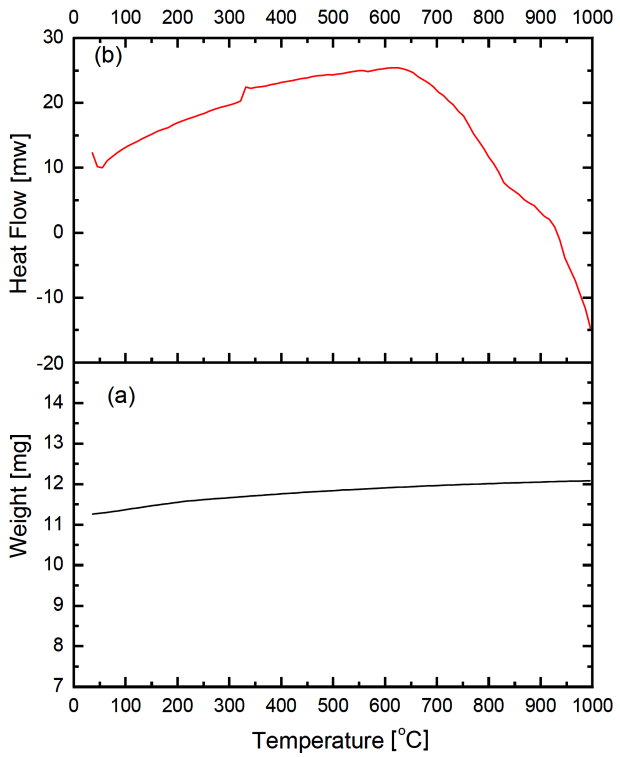

Figure 1. TG (a) and DSC curves (b) of TiO_2

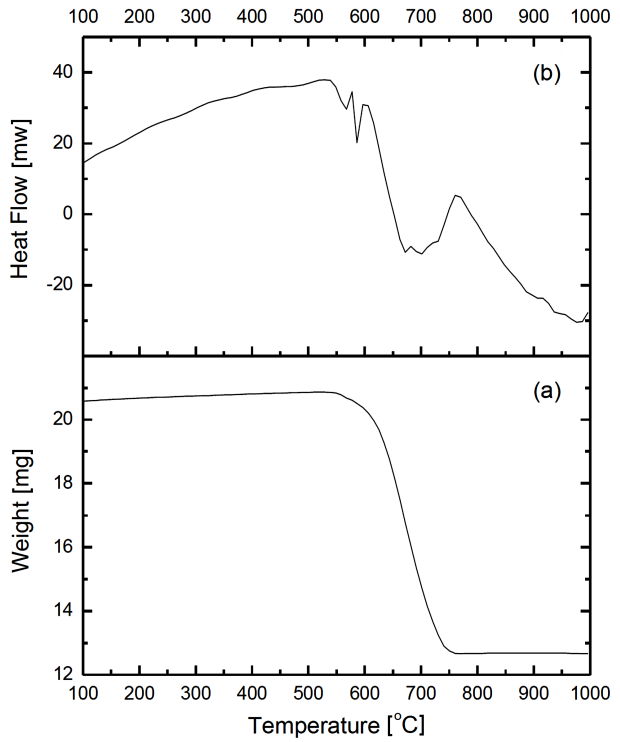

Figure 2. TG (a) and DSC curves (b) of $Ba(NO_3)_2$

materials. Equi-molar amounts of $Ba(NO_3)_2$ and TiO_2 powders were crushed in agate mortar for 3 hours. The mixture was transferred to an alumina crucible and calcined in a furnace (Matrix, India) at 800 °C for 8 h with a heating rate of 10 °C/min and after that the furnace was cooled down to room temperature.

2.2. Characterization techniques

Thermal analysis (TG and DSC) of the reactants, precursor mixture of reactants and synthesized powders were carried out by using simultaneous TG-DSC (Metller Toledo, Germany) thermal analyzer in the temperature range 30–1000 °C with heating rates of 10 and 20 °C/min in nitrogen atmosphere. A preliminary study on compound formation and lattice parameters was carried out by using X-ray diffraction (XRD) technique with an X-ray powder diffract meter (Miniflex, Rigaku). Fourier transform infrared (FTIR) spectra of the sample were recorded by using Fourier Transform Infra-red Spectrometer (Shimadzu, Model DF 803) in the wave number range 400–4000 cm^{-1}.

III. Results and discussion

3.1. Thermal analysis of TiO_2 and $Ba(NO_3)_2$

The TG and DSC curves of TiO_2 powder with a heating rate of 10 °C/min in nitrogen atmosphere are shown in Figs. 1a and 1b, respectively. No weight change and peaks have been observed in the TG and DSC curves of TiO_2 powder in the temperature range 30–1000 °C.

The TG and DSC curves of $Ba(NO_3)_2$ are shown in Figs. 2a and 2b, respectively. The TG curve shows a single step weight loss (approximately 41%) in the temperature range 550–725 °C. It was reported [13] that anhydrous bulk barium nitrate decomposes over the temperature range 500–700 °C, with the main decomposition taking place at 630 °C. Slightly higher decomposition temperature range observed for nitrate used in this work may be due to difference in the particle size. The observed weight loss is in good agreement with the theoretical weight loss calculated according to the reaction (1):

$$Ba(NO_3)_2 \longrightarrow BaO + 2\,NO_2 + 0.5\,O_2 \qquad (1)$$

The DSC curve of $Ba(NO_3)_2$ shows two peaks at 587 °C and 708 °C. The first peak is attributed to the melting of $Ba(NO_3)_2$ whereas the second peak to the decomposition of $Ba(NO_3)_2$ to BaO according to the reaction (1). The observed melting temperature is approximately the same as reported value of 592 °C [14].

3.2. Thermal analysis of $Ba(NO_3)_2/TiO_2$ mixture

Figures 3 and 4 show the TG and DSC curves, respectively, of the mixture of $Ba(NO_3)_2$ and TiO_2 obtained upon heating with two different rates (10 and 20 °C/min) and for two different mixing times (1 and 3 hours). There is no significant change in the nature of TG curves with variations in the heating rate and mixing time. All three TG curves show a single step weight loss (approximately 31%) between 550–625 °C. The formation of $BaTiO_3$ perovskite phase, in single step accompanied by the release of NO_2 and O_2 gases, takes place according to the following equation:

$$Ba(NO_3)_2 + TiO_2 \longrightarrow BaTiO_3 + 2\,NO_2 + 0.5\,O_2 \qquad (2)$$

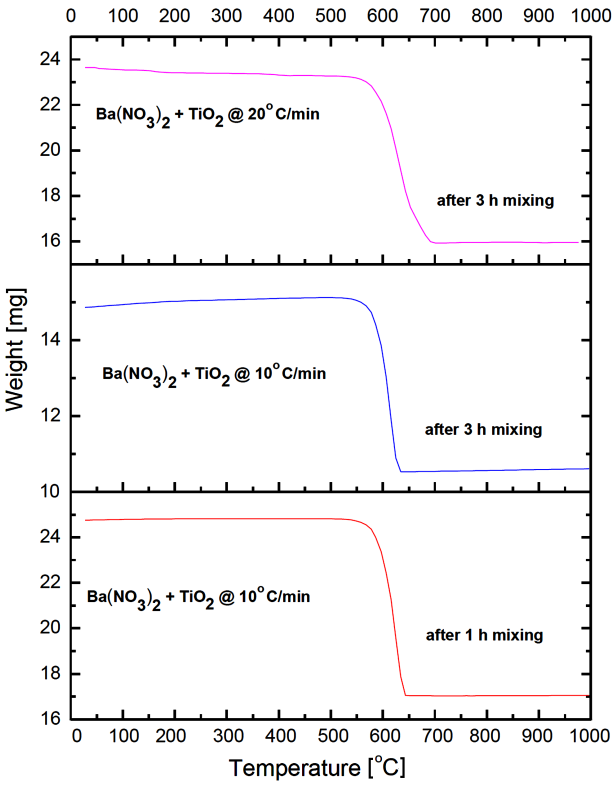

Figure 3. TG curves (obtained with different heating rates) of the mixture of $Ba(NO_3)_2$ + TiO_2 prepared by different mixing times

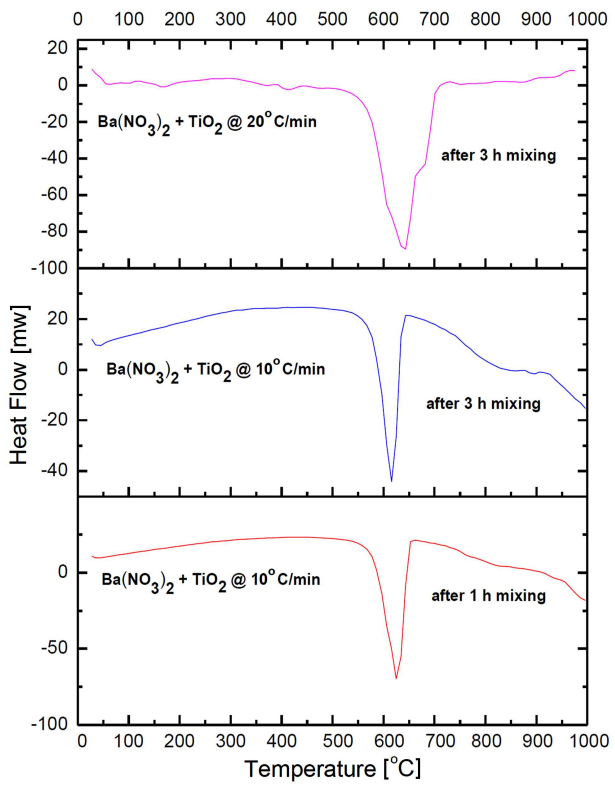

Figure 4. DSC curves (obtained with different heating rates) of the mixture of $Ba(NO_3)_2$ + TiO_2 prepared by different mixing times

The weight loss of 31% observed experimentally is in agreement with the theoretical weight loss calculated according to the reaction (2).

DSC curves show only one endothermic peak between 610–650 °C. Since this peak is above the melting temperature of $Ba(NO_3)_2$ it is attributed to the liquid-solid reaction between $Ba(NO_3)_2$ and TiO_2 during the formation of $BaTiO_3$. Observations of a single peak in the DSC curve contradict to the results reported by other workers. Tagawa *et al.* [10] have observed two endothermic peaks in the DTA curve. They attributed the first peak, at ~600 °C, to the melting of $Ba(NO_3)_2$ and the second one, at ~650 °C, to the reaction of $Ba(NO_3)_2$ with TiO_2. They concluded that the reaction occurs in the liquid-solid phase after the melting of $Ba(NO_3)_2$ at high heating rates (10 and 20 °C/min). Othman *et al.* [12] showed that the reaction between $Ba(NO_3)_2$ and TiO_2 proceeds during heating up in three consecutive stages, characterized by three endothermic peaks at 605, 633.7 and 675.2 °C in the DTA curve. The first peak (at 605 °C) might be attributed to the solid-solid reaction between $Ba(NO_3)_2$ and TiO_2 powders. The second peak (at 633.7 °C) is due to the reaction between the partially melted $Ba(NO_3)_2$ and TiO_2. The last endothermic peak (at 675.2 °C) is due to the complete reaction of the molten $Ba(NO_3)_2$ with the residual TiO_2.

3.3. Characterization of synthesized $BaTiO_3$ powder

Figure 5 shows TG-DSC curves of the synthesized $BaTiO_3$ powder, obtained after calcination at 800 °C for 8 h at a heating rate of 10 °C/min in nitrogen atmosphere. The TG curve depicts only 0.4% weight loss below 800 °C which could be attributed to the decomposition of a small amount of an impurity phase. There is no distinct peak in the DSC curve of the obtained powder which reflects high purity and thermal stability of the synthesized material.

The X-ray diffraction (XRD) pattern of synthesized $BaTiO_3$ powder is shown in Fig. 6 and confirms the formation of $BaTiO_3$. The crystal structure of $BaTiO_3$ powder is tetragonal (JCPDS No. 15-0780) because both 200 and 002 peaks (around 2θ = 45°) are present in the XRD pattern (see the inset of Fig. 6). The lattice parameters obtained using software "Cell" are a = 3.9950±0.0003 Å and c = 4.0318±0.0004 Å. The value of the tetragonality calculated using these values of lattice parameters is 1.0092 which is slightly smaller than standard value 1.0110. This may be due to the lower synthesis temperature used. It is reported that tetragonality of $BaTiO_3$ is a function of temperature and standard value of tetragonality can be achieved after sintering at temperature >1300 °C [15].

The average crystallite size of the synthesized $BaTiO_3$ powder was calculated from the X-ray line broadening of the 110 peak using Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta_{max}} \tag{3}$$

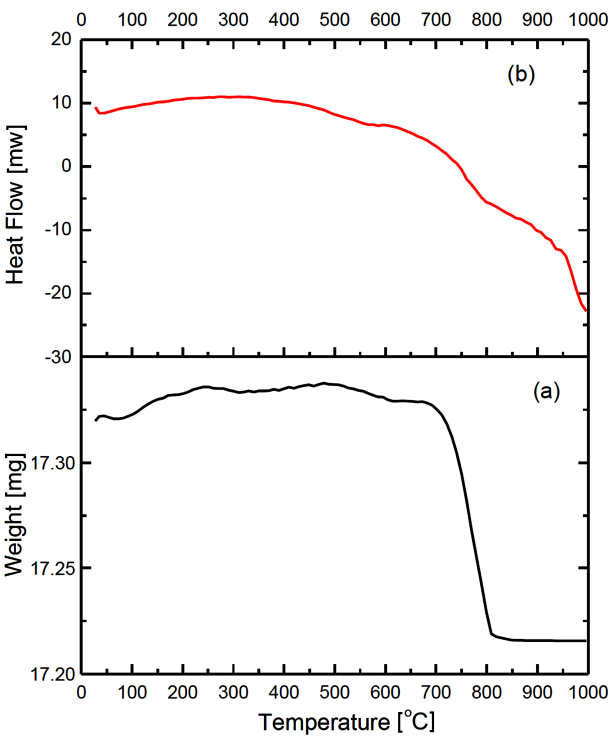

Figure 5. TG (a) and DSC curve (b) of synthesized $BaTiO_3$ powder

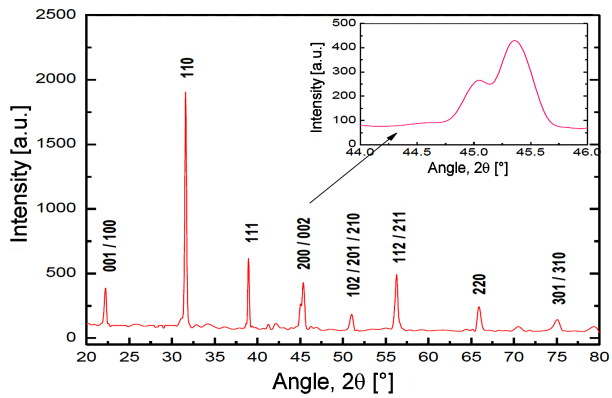

Figure 6. X-ray diffraction pattern of synthesized $BaTiO_3$ powder

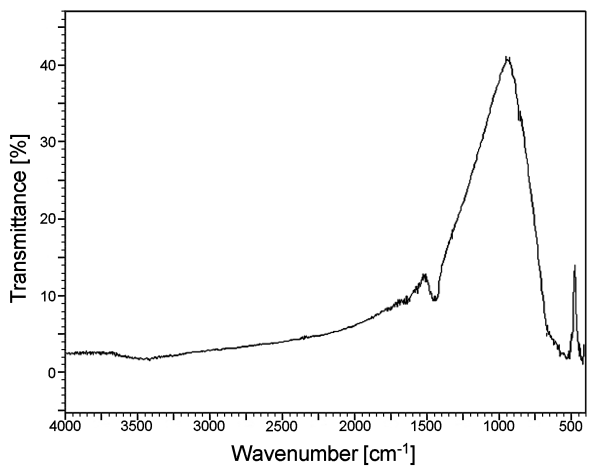

Figure 7. FTIR spectrum of synthesized $BaTiO_3$ powder

where D is the average grain size, λ = 1.541 Å (X-ray wavelength), and β is the width of the diffraction peak at half maximum for the diffraction angle 2θ. The average particle size is found to be 44 nm.

According to the reported literatures, $BaCO_3$ is the most common impurity of the $BaTiO_3$ powder prepared by any method. FTIR was found to be the most sensitive technique for the detection of $BaCO_3$. On the basis of FTIR analysis, $BaCO_3$ concentration down to 0.6% has been estimated. In order to check the purity of the obtained $BaTiO_3$ powder, FTIR spectra of the sample is recorded and shown in Fig. 7. The crystallization of barium titanate was confirmed by the broad band centered at 540 cm^{-1}, which is typical of the Ti–O stretching vibrations in $BaTiO_3$, and also by the second broad band observed at the end of the spectra, below 500 cm^{-1}, corresponding to the Ti–O bending vibrations [16]. The very small absorption band at 1440 cm^{-1} can be interpreted as C=O vibration due to extremely small unavoidable traces of carbonate [17]. This result is contradictory to the result obtained by XRD (Fig. 6 in which no peak of $BaCO_3$ is observed), but is in agreement with results obtained by TG curve (Fig. 5). From the TG it was found that amount of impurity phase $BaCO_3$ is approximately 0.4% and as it could be expected XRD is unable to detect such small amount of $BaCO_3$ impurity phase.

IV. Conclusions

The $BaTiO_3$ powder was synthesized from $Ba(NO_3)_2$ and TiO_2 powder mixture with 1:1 molar ratio. The TG-DSC results showed that the reaction between $Ba(NO_3)_2$ and TiO_2 proceeds during heating up in single stage (above 600 °C) between molten $Ba(NO_3)_2$ with TiO_2 (liquid-solid reaction). The TG-DSC results showed that the formation of $BaTiO_3$ phase from $Ba(NO_3)_2$ and TiO_2 powder mixture takes place before $Ba(NO_3)_2$ decomposes to BaO. X-ray diffraction pattern of the synthesized $BaTiO_3$ obtained after calcining mixture of $BaTiO_3$ and TiO_2 at 800 °C for 8 h confirmed the formation of tetragonal phase with lattice parameters a = 3.9950±0.0003 Å and c = 4.0318±0.0004 Å. The obtained powder has crystallite size of 44 nm. The purity of the obtained powder has been checked by thermal characterization (TG and DSC). Only 0.40% weight loss has been detected within temperature range 40–1000 °C. This small amount of impurity phase was identified as $BaCO_3$ using Fourier transform infra-red (FTIR) technique.

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