

Synthesis of BaTiO₃ powder from barium titanyl oxalate (BTO) precursor employing microwave heating technique

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Abstract. Cubic barium titanate (BaTiO₃) powder was synthesized by heating barium titanyl oxalate hydrate, BaTiO(C₂O₄)₂·4H₂O (BTO) precursor in microwave heating system in air at 500°C. Heating BTO in microwave above 600°C yielded tetragonal form of BaTiO₃. Experiments repeated in silicon carbide furnace showed that BaTiO₃ was formed only above 700°C. The product obtained was cubic.

Keywords. Ceramics; electronic materials; ferroelectrics; perovskites; microwave synthesis; BaTiO₃.

1. Introduction

Barium titanate (BaTiO₃), a high-tech material used for the manufacture of capacitors and sensors is the first of the ceramic type ferroelectrics to be discovered and has been most extensively studied (Mc Quarrie 1955). Doped BaTiO₃ is a strategic material used in different electroceramic devices (Iwaya *et al* 1983).

Different methods of synthesis of BaTiO₃ are reported in the literature. These include (i) conventional ceramic methods (Rase and Roy 1955), (ii) sol gel processes (Hench and Ulrich 1986; Shimooka *et al* 2000), (iii) modified alkoxide synthesis (Phule and Risbud 1989) and (iv) chemical co-precipitation methods (Clabaugh *et al* 1956; Potdar *et al* 1992, 1998; Kholam *et al* 2002). The temperature of synthesis of BaTiO₃ by conventional ceramic technique is relatively higher (> 1200°C) compared to those observed in other methods (Rase and Roy 1955). In a recent publication, Agrawal and co-workers (Agrawal 1998) described the synthesis of BaTiO₃ from the mixture of barium carbonate and titanium dioxide employing microwave heating. They observed that hypostoichiometric TiO₂ (TiO_{2-x}) reacted with BaCO₃ in the presence of microwave field at temperature as low as 350°C to give the mixture of hexagonal and tetragonal forms of BaTiO₃. Increasing the temperature above 800°C transformed the hexagonal phase in the mixture completely to the tetragonal form. The same mixture heated in normal resistance furnace could not yield BaTiO₃ but produced Ba₂TiO₄ above 900°C. It was further observed that a mixture of BaCO₃ and stoichiometric TiO₂ heated in microwave up to 900°C produced

only Ba₂TiO₄. Heating the same mixture above 1100°C in microwave resulted in the formation of the mixture of Ba₂TiO₄ and tetragonal form of BaTiO₃. The increased reactivity of non stoichiometric TiO₂ was attributed to the most efficient interaction of TiO_{2-x} (which has anion vacancies) with the microwave field (Agrawal 1998).

The observations of Agrawal and co-workers prompted us to synthesize BaTiO₃ powder from the precursor which would generate non stoichiometric TiO_{2-x} *in situ*. This would eliminate the need for reduction of titanium dioxide prior to the heat treatment of the mixture of reactants in the microwave field. In the present paper we attempted to synthesize BaTiO₃ by heating BTO in microwave heating system. It was felt that the carbon monoxide released during the thermal decomposition of BTO would provide reducing atmosphere to maintain non stoichiometry in the titanium oxide formed during the reaction. BaTiO₃ in the cubic form could be synthesized at temperature as low as 500°C within an hour using this method. Further heating above 600°C induced transformation in the product from cubic to tetragonal form.

2. Experimental

2.1 Synthesis of barium titanyl oxalate (BTO)

BTO used in the present work was synthesized from the aqueous solution of Ba(NO₃)₂ (BN) and K₂TiO(C₂O₄)₂ (KTO). Both the chemicals were of AnalaR grade. The method consisted of mixing of equimolar aqueous solutions of BN and KTO with constant stirring. The white BTO precipitate obtained was filtered, washed with distilled water and dried in an oven at 50°C for 24 h. From chemical analysis, the product could be assigned the molecular formula, BaTiO(C₂O₄)₂·4H₂O.

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2.2 Thermogravimetry (TG), differential scanning calorimetry (DSC) and differential thermal analysis (DTA)

The (TG) as well as (DSC) curves for BTO was recorded in flowing argon at the heating rate of 10°C/min on 9.6 mg sample, employing simultaneous recording TG/DSC SETARAM system (Model 92-16). In addition, differential thermal analysis (DTA) plot for thermal decomposition of BTO was recorded in flowing air at the heating rate of 10°C/min using the instrument supplied by Universal Thermal Analysis Instruments, Mumbai, built to our specifications.

2.3 Preparation of barium titanate (BaTiO₃)

The BTO precursor was heated to different temperatures in the range 400–700°C employing the microwave heating system fabricated indigenously. The details of microwave system used in the present study are described elsewhere (Borkar and Dharwadkar 2004). The microwave oven used could supply maximum 750 watts input power. The power to the unit could be maintained to a constant set value to fix the desired temperature needed for the experiments, employing the proportional type (PID) temperature controller coupled to a solid state relay (SSR). A shielded chromel–alumel thermocouple was used as a sensor for controlling the input power to the microwave oven at the set temperature. The thermocouple shield had to be grounded to obtain steady temperature values at the set point. The temperature of the sample could be maintained constant to ± 1°C and measured by a separate calibrated chromel–alumel thermocouple. The influence of microwave field on the measured temperature, if any, was checked by momentarily putting off the microwave oven. No difference was observed in the temperature displayed on the indicator. The sample contained in a cylindrical zirconia crucible was surrounded symmetrically by four silicon carbide rods, which acted as a preheater for the samples poorly interacting with the microwaves at ambient temperature. A schematic of the microwave heating system used in this investigation is shown in figure 1.

The products obtained after heat treatment of reactants at different temperatures were analysed by X-ray diffraction using SIEMENS X-ray diffractometer (Model D-500) at the scanning speed of 1°2θ/min. A monochromatized X-ray beam of wavelength 1.5405 nm was used.

3. Results

3.1 Thermogravimetry (TG), differential scanning calorimetry (DSC) and differential thermal analysis (DTA) of BTO

TG and DSC plots recorded for BTO are shown in figure 2. TG curve (figure 2a) shows sequence of four steps with different mass losses involving dehydration and decarboxy-

lation. The resulting final product has the stoichiometry corresponding to BaTiO₃. The DSC plot for the decomposition recorded in argon (figure 2b) shows four endothermic peaks corresponding to the reactions (1), (2), (3) and (4). The DTA curve recorded in air (figure 3), shows an endothermic peak followed by a predominately exothermic peak and a sequence of two minor endothermic peaks. From the TG and DTA results it is concluded that the formation of BaTiO₃ in air involves the following sequence of steps

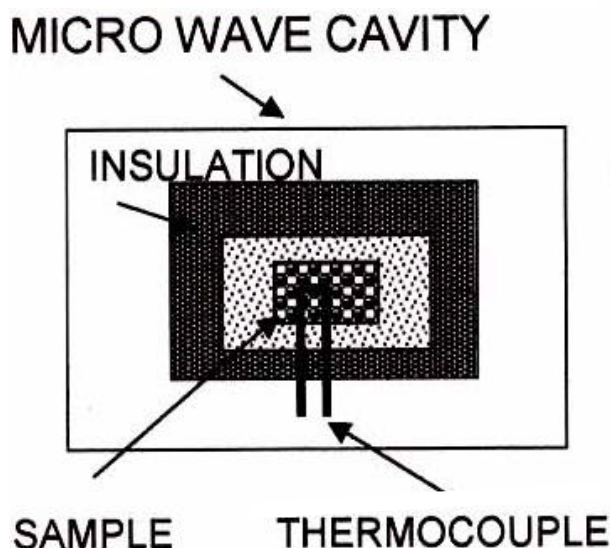
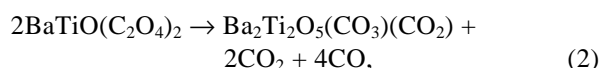


Figure 1. Schematic of microwave heating system.

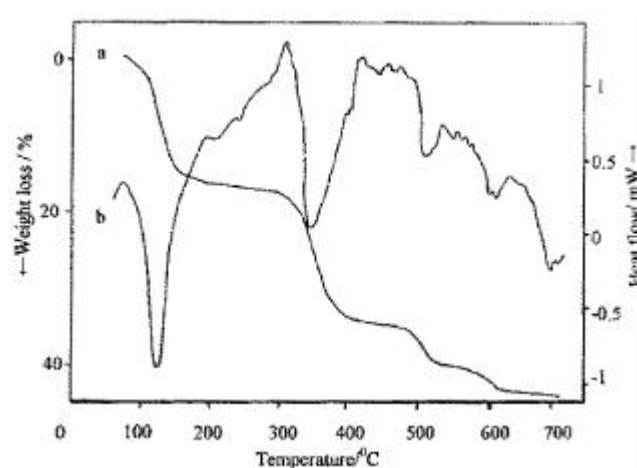
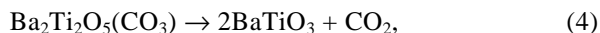


Figure 2. TG (a) and DSC (b) curves of BTO recorded in argon atmosphere.



The steps representing the formation of BaTiO₃ from BTO concluded from the present studies are identical to those reported by Gopalkrishnamurthy and coworkers (1975).

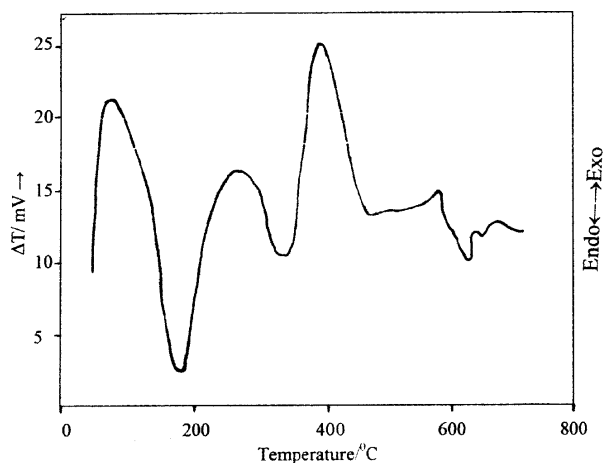


Figure 3. DTA curve of BTO recorded in air.

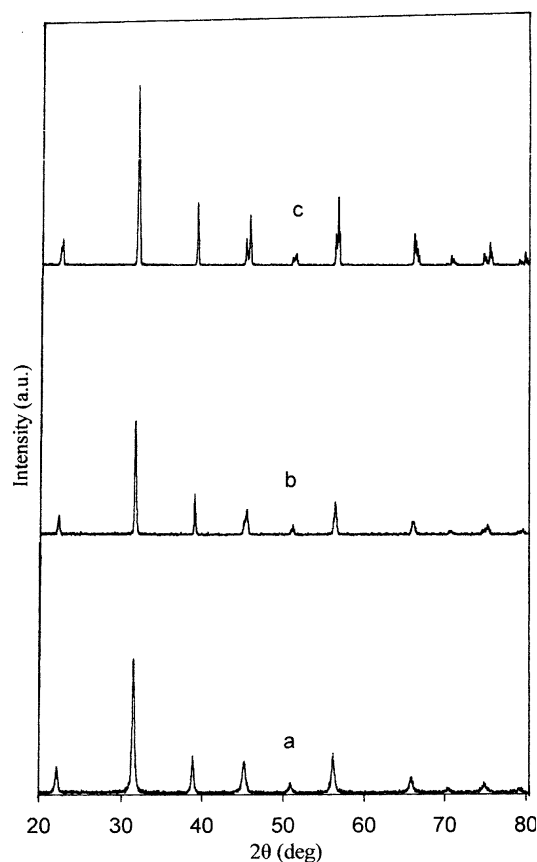


Figure 4. XRD patterns of BTO calcined in microwave heating system at (a) 500, (b) 600 and (c) 700°C for 1 h.

It could be concluded from the TG curve that the formation of BT from the precursor was complete by 600°C. It is interesting to note that in the second step of decomposition of BTO carbon monoxide is evolved as the gaseous product which could provide reducing atmosphere in the vicinity of the sample.

3.2 X-ray diffraction patterns

The X-ray diffraction patterns of the product of thermal decomposition of BTO in microwave heating system in the temperature range 500–700°C are presented in figure 4. It is observed that formation of BaTiO₃ from BTO is complete at 500°C. The product at 500°C consists of pure cubic BaTiO₃. The product obtained at 600°C, however, indicates that the cubic form possibly transforms to tetragonal structure as revealed by asymmetry introduced in peaks at the 2θ values corresponding to 45.25, 50.90, 56.12, 74.87 and 79.5, respectively. The splitting of these peaks in the sample heated at 700°C and above confirmed the transformation of cubic phase to a tetragonal form.

4. Discussion

The results presented in the foregoing sections indicate that BaTiO₃ in the cubic form could be synthesized by heating BTO at temperature as low as 500°C. The reducing atmosphere provided by the evolved carbon monoxide (2) could perhaps be responsible to yield non stoichiometric TiO₂ which subsequently reacted at low temperatures to form BaTiO₃. The product obtained began to transform to

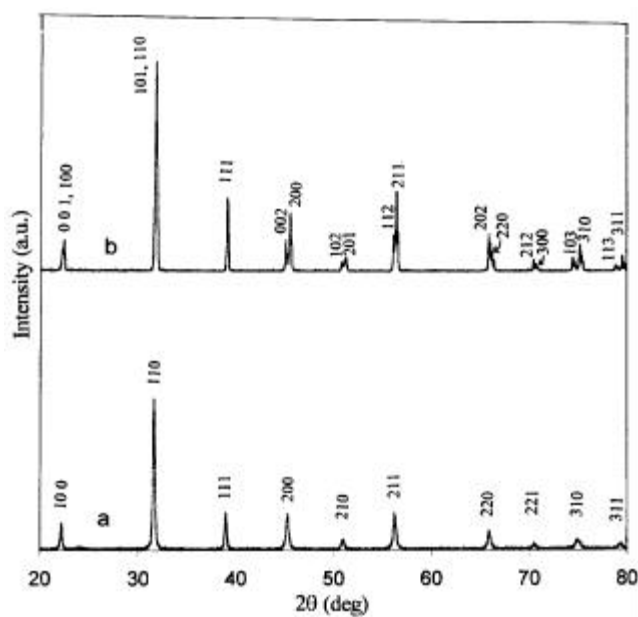


Figure 5. XRD patterns of BTO calcined in (a) silicon carbide furnace and (b) microwave heating system at 700°C for 1 h.

the tetragonal phase above 600°C. The transformation was complete at 700°C. This is revealed by splitting of several lines present in the X-ray pattern of the cubic phase into doublets, mentioned earlier.

The other important aspect which emerged from this investigation is the fact that BTO precursor on decomposition in air yielded pure product, BaTiO₃ at 700°C irrespective of mode of heating. The crystallographic forms obtained in the two cases are, however, different (figure 5). The product obtained by heating the BTO precursor in silicon carbide furnace at 700°C in air was cubic. BaTiO₃ could not be, however, obtained in any crystallographic form by heating BTO in silicon carbide furnace in air below 650°C.

Our present observations indicate that the lowering of reaction temperature in microwave heating could be the result of two independent factors, which, besides the interaction of microwave with defects, could also involve the role of oxygen vacancies in solid state reaction. This is borne out from the fact that at 700°C the BTO transforms to BaTiO₃ even in the absence of microwave field. It is felt that evolution of CO in the decomposition of BTO creates reducing atmosphere in the vicinity of the sample which could be sufficient to yield hypostoichiometric TiO₂ facilitating the solid state reaction at much lower temperature.

5. Conclusions

The results obtained in this investigation show that BaTiO₃ in the cubic form could be synthesized from BTO at temperature as low as 500°C. Thermal decomposition of BTO presumably yields hypostoichiometric TiO₂ by virtue of the presence of evolved CO in the reaction, which in the presence of the microwave field combines with BaO to yield the cubic phase. The cubic BaTiO₃ transformed completely to the tetragonal form on heating it in the microwave field above 700°C.

In the recent studies (Potdar *et al* 1998; Khollam *et al* 2002), it was reported that BTO on heating in the resis-

tance heated furnace above 700°C in air produced cubic form of BT. Our present observations are in agreement with these results. The cubic form was transformed to tetragonal structure in the pellets sintered in air above 1250°C (Potdar *et al* 1998; Khollam *et al* 2002). The production of tetragonal form of BaTiO₃ at low temperatures following the present procedure could provide considerable edge over other existing processes and make it economically much more viable for commercial exploitation.

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