


## Preparing of Barium Titanate Using Chemical Method and Studying of its Structural Properties

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Received on: 20/9/2011 & Accepted on: 7/6/2012

### ABSTRACT

Single crystalline BaTiO<sub>3</sub> (BT) was prepared using TiCl<sub>4</sub>, BaCl<sub>2</sub> and oxalic acid. The structure of the prepared nanocrystalline BT powders were a tetragonal perovskite according to XRD and HRTEM analysis. Annealing powder to 750°C show that pure BT phase was formed according to XRD, TG, and FTIR spectroscopy. The TEM images of the prepared powder reveal spherical morphology of BT, while a finger twin, dendritic and embryo shape are observed of BT powder calcined at 230, 530, and 750°C respectively. SAED and HRTEM images showed a high crystalline BT powder and a single crystalline BT respectively.

**Keywords:** Single crystal, Finger twin, Dendritic, BaTiO<sub>3</sub>.

### تحضير مادة باريوم تيتانيت بالطريقة الكيميائية ودراسة خصائصها التركيبية

#### الخلاصة

تم تحضير باريوم تيتانيت احادي التبلور باستخدام (TiCl<sub>4</sub>) و (BaCl<sub>2</sub>) بطريقة حامض الاوكزاليك. اظهرت نتائج الدراسة بان مادة الباريوم تيتانيت ذات طور رباعي وذلك عن طريق تحليلات الـ (XRD) و (HRTEM). وكذلك من خلال حرق المسحوق الناتج الى درجة 750 ظهر المسحوق بشكله النقي. الصور المأخوذة لمسحوق الباريوم تيتانيت (TEM) اظهرت كروية الشكل عند حرقه الى درجة 230، بينما تغيرت اشكاله الى اصابع توأمية، واشكال شجيرية وجنينية عند حرقه عند درجة 530 و 750 على التوالي.

## INTRODUCTION

**B**arium Titanate (BT) is a first developed piezoelectric ceramic with perovskite ( $ABO_3$ ) structure that finds many applications in electronics devices [1, 2, 3]. It is actually attractive for a variety of applications including: nonvolatile ferroelectric memories, microwave devices, dynamic random access memories (DRAMs), multilayer capacitors, microelectromechanical systems (MEMS), pyroelectric detectors, piezoelectric actuators [4]. At room temperature, its electrical resistivity is highly but it can be dramatically lowered by some dopants [5], or with grain size decreasing [6, 7, 8]. BT can be prepared by two different techniques (conventional and wet chemical synthesis), both have a large effects on each composition and properties of the resultant powder. The second technique is preferred due to its homogeneous, spherical, and stoichiometric BT, moreover this techniques not expensive, need no high temperature and nor long time, just controlled preparation of mixed row materials [9, 10]. As example of wet chemical techniques: BT in many investigations synthesized by using hydrothermal method [11-14], carbonate-oxalate, gel-carbonate and gel- to-crystallite conversion [15], even it prepared by solid state reaction [16]. Many researchers studied the influence of various preparation parameters such as: reaction time, temperature, pH value, and Ba/Ti ratio on formation of BT by chemical synthesis [17, 18]. The present study is focusing on the effect of chosen synthesis and calcined temperature on the structural of prepared BT powder.

## EXPERIMENTAL PROCEDURE

Grade reagents  $BaCl_2 \cdot 2H_2O$ ,  $TiCl_4$ , were used as the initial raw materials; the purity of all raw materials is more than 99%. First step begin when dissolved 1 mole of  $BaCl_2 \cdot 2H_2O$ , and 1 mole of  $TiCl_4$  in distilled water at least for 30 minutes, then 3 mole of oxalic acid solution add to the first solution slowly with stirring. The resultant precipitate dried and calcined at three different temperatures. At last each of a spectroscopic analysis includes X-ray-diffraction (D/Max-RB Model), TEM (JEM-100SX NEC) and thermals analysis (FTIR (Spectrum one PE) and TG (American PE Co.)) tested for the formation BT powders.

## RESULTS AND DISCUSSIONS

Figure (1) represents the weight loss of BT powders as a function of temperature. It can be seen from Fig (1), there are three ranges where the weight loss of BT powder were investigated. Firstly between room temperature to  $200^\circ C$ , secondly between  $200^\circ C$  to  $350^\circ C$  and finally between  $350^\circ C$  to  $700^\circ C$ . These losses correspond to the loss of hydroxyl and carbonate groups respectively. After  $700^\circ C$ , BT powder do not undergo any weight loss and that mean BT prepared powder are empty from any defects and all the interaction processes full filled close to this temperature. Fig (1) also shows three different stable regions were assigned at 200-250, 500-550, and  $700^\circ C$ . To understand the structure of BT powders, XRD is performed at these three stable regions.

The preparation of  $BaTiO_3$  has been the subject of a number of papers, several of them state in their original paper that when a solution of  $BaCl_2$  is added to solution of  $TiCl_4$  and oxalic acid at  $80^\circ C$ . A precipitate forms immediately, which

dissolved and precipitates as BTO ( $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ ). In this effort this precipitate is clearly observed in Fig (2a) which demonstrated to the XRD patterns of prepared powder at 230°C. In Fig (2b) a characteristic diffraction peaks could be discerned when calcined powder at 530°C, these peaks assigned as a minor impurity phases. These phases were not detected with increase in calcination temperature to 750°C as be seen in Fig (2c) which indicated complete reaction of  $\text{TiO}_2$  powder under preparing conditions.

By using scherrer's formula the grain size according to ( $d_{110}$ ) peak equal to 30 nm and the lattice constant ( $a$ ) (0.49) nm, the lattice constant is agreed very well with that reported in the literatures as the standard value (JCPDS) which revealed that a tetragonal phase was formed.

In the previous results, there are some impurities incorporate inside the lattice of BT particles as shown in XRD results, to investigate about these impurities, FTIR analysis is down. Fig (3) shows the FTIR spectra of as prepared BT powders calcined at 230°C, 530°C, 750°C. In Fig (3a) and (3b) abroad band region of 3000-3429 $\text{cm}^{-1}$  assigned to the starching mode of internal OH- ions, moreover, little board band observed at region 1411-1683  $\text{cm}^{-1}$  assigned to bridged oxalate species. The broad band of 1500-1750 $\text{cm}^{-1}$  assigned to carbonate groups and 804 $\text{cm}^{-1}$  to  $\text{BaCO}_3$ , 528 $\text{cm}^{-1}$  band assigned to standard BT[12]. Fig(3c) illustrates for each calcined powders at 750°C, was detected to the released of most of hydroxyl groups at 750°C.

The TEM images of as prepared BT powders demonstrated in Fig.(4). Fig.( 4a) revealed that the spherical aggregates composed of many tiny particles with 50-80 nm in diameter (in agreement with result of XRD), which tend to form as finger twin, dendrite, and embryo after calcined at 230°C, 530°C, and 750°C as shown in Fig.(4b), (4c), and (4d) respectively.

Figure 4e shows the Selection Area Electron Diffraction (SAED) pattern recorded from arbitrary spherical in Fig. 4a, which demonstrates good crystallinity comes from the regular spots and coordination.

Figure (4g), (4h), (4i) depict the High Resolution TEM (HRTEM) images taken from Fig. 4f and a randomly chosen finger twin, which show that lattice structures at the tip of the finger. The lattice fringes of HRTEM images were examined to be 2.84 nm which close to the (110) lattice spacing of the tetragonal BT as shown in Fig. (2c). These images revealed the BT dendrites are in single crystal because all of them have the same interplanar spacing.

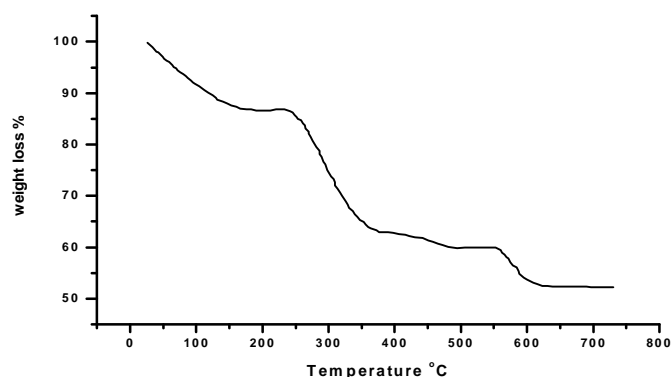
## CONCLUSIONS

Nanocrystalline BT powders have been prepared by oxalate method as a result of the reaction between  $\text{TiCl}_4$  and  $\text{BaCl}_2$  in oxalic acid. XRD results indicate that the BT nanocrystals remain a metastable cubic structure at room temperature and convert a tetragonal when calcined powder at 750°C. Hydroxyl and carbonate groups were observed in prepared powders which showed in FTIR spectroscopy as vibrational bands and TG as weight loss. The crystallite size was 50-80 nm as a shown in XRD and TEM images. The lattice fringes of HRTEM images were examined to be 2.84 nm which close to the (110) lattice spacing of the tetragonal BT, therefore TEM images revealed that the BT dendrites are in single crystal.

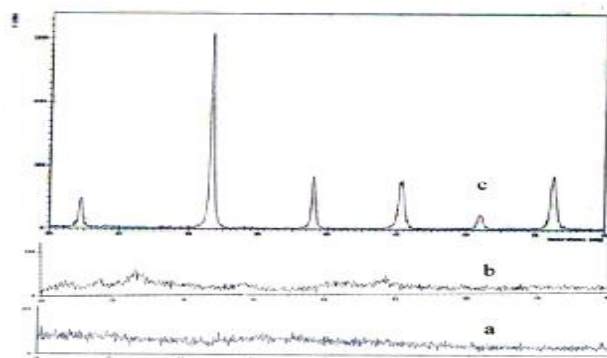
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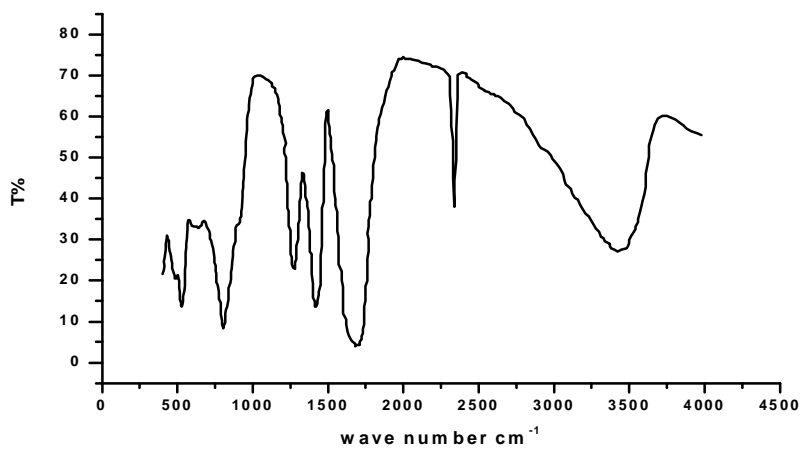
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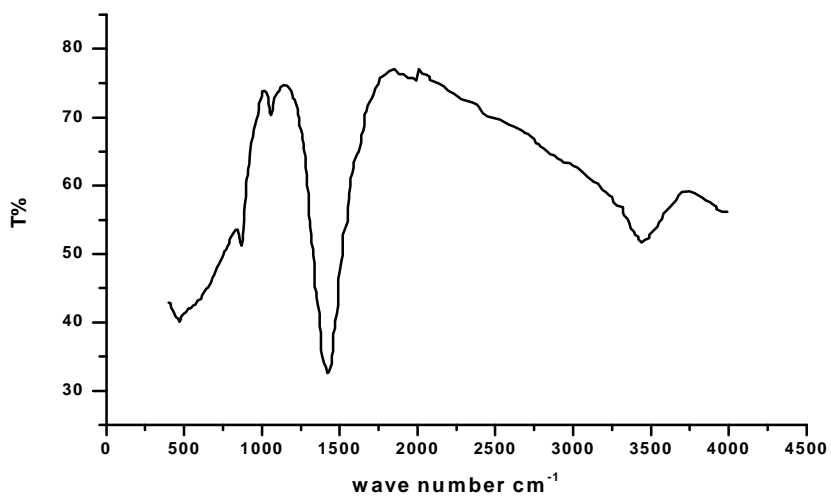
**Figure (1) TG analysis of BT powders.**



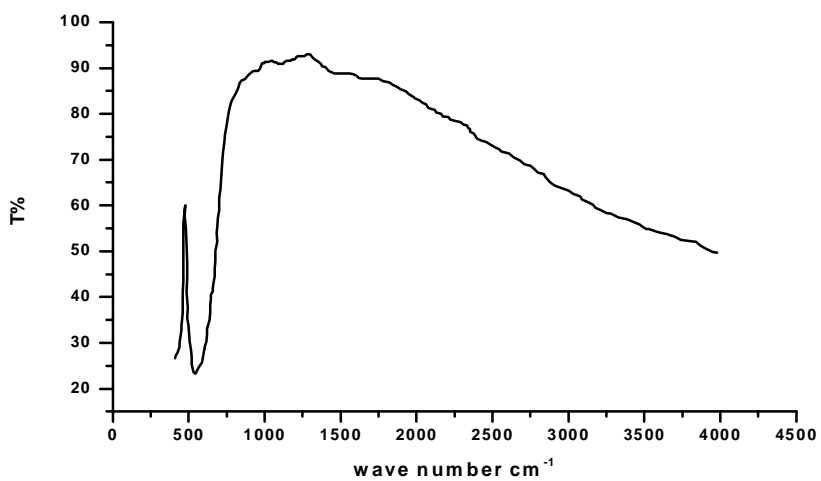
**Figure (2) XRD pattern of BT powders at a) 230°C, b) 530°C and c) 750°C.**



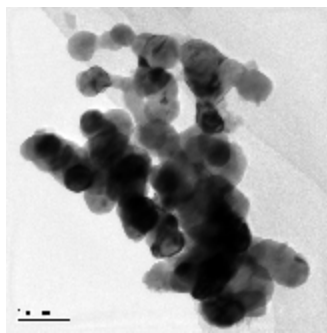
**Figure (3 a)**



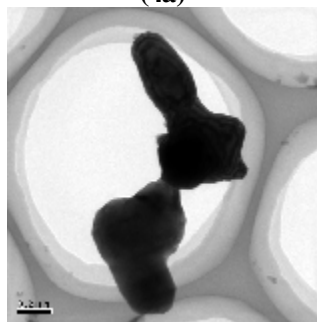
**Figure (3 b)**



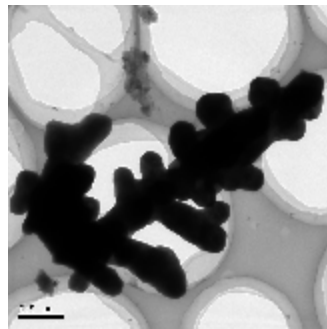
**Figure (3 c)**  
**Figure (3) FTIR spectroscopy of BT powders at a) 230°C, b) 530°C and c) 750°C.**



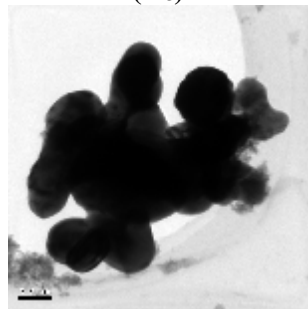
**(4a)**



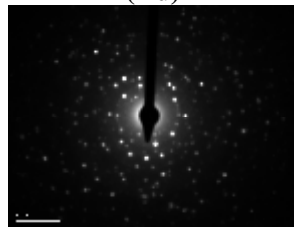
**(4b)**



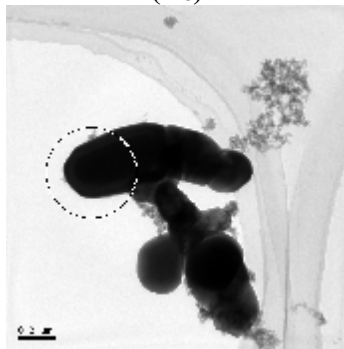
**(4 c)**



**(4 d)**

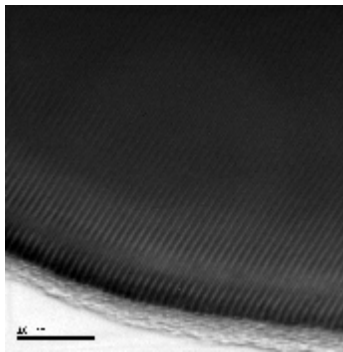


**(4 e)**

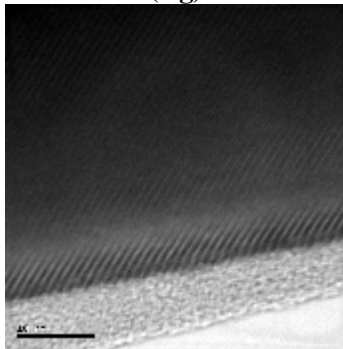


**(4 f)**

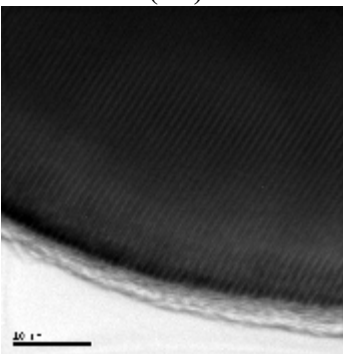




**(4 g)**



**(4 h)**



**(4 i)**

**Figure (4) TEM images of BT powders at a) room temp., b) 230°C, c) 530°C and d) 750C,e) SAED of BT powers, g, h and i) HRTEM images taken from f.**