

## Application of Statistical Design to Optimize the Preparation of Barium Titanate Nanopowders via Oxalate Precursor Method

M.M. Rashad<sup>1\*</sup>, R.S. Mohammed<sup>1</sup>, A.A. El-Midany<sup>1</sup>, A.T. Kandil<sup>2</sup> and I.A. Ibrahim<sup>1</sup>

<sup>1</sup>Central Metallurgical Research and Development Institute, P.O. Box: 87 Helwan, 11421 Cairo, Egypt

<sup>2</sup>Inorganic & Nuclear Chemistry Dept., Faculty of Science, Helwan University, Cairo, Egypt

### Abstract

Nanocrystalline barium titanate ( $\text{BaTiO}_3$ ) powders have been synthesized by oxalate precursor method. Statistical design (Box-Behnken) is used to study the effect of main three parameters: calcination temperature (800-1200°C), calcination time (0.5-4 hrs), and oxalic acid mole ratio (0.5-1.5) related to barium and titanium added at constant Ba/Ti mole ratio 1 on the formation of BT powders. Barium titanate particles were characterized using X-ray diffraction (XRD), and scanning electron microscope (SEM). The statistical design showed that conversion of barium titanate increases by decreasing the oxalic acid mole ratio and decreasing the calcination temperature and calcination time. XRD showed that single phase of barium titanate is formed at calcination temperature starting from 800°C, oxalic acid mole ratio 0.5 and calcination time 2.25 hrs. The average crystallite sizes at different conditions are in the range between 36 to 91 nm. SEM micrographs showed that the produced pure BT nanopowders were formed in the tetragonal structure shape.

### Introduction

Barium titanate  $\text{BaTiO}_3$ , (BT) is a typical ferroelectric, piezoelectric, and insulating material with a perovskite oxide structure  $\text{ABO}_3$ . It has potential commercial applications due to its high permittivity, high dielectric constant, low dielectric loss, high breakdown voltage and excellent volumetric efficiency of the capacitance [1-2]. BT is used mainly in multilayer ceramic capacitors (MLCCs), chemical sensors, PTC thermistors, piezoelectric devices like underwater transducers, capacitance in printed circuit boards (PCB) and non volatile memories. MLCCs with a dielectric thickness of 2  $\mu\text{m}$  have already been commercialized but the next generation components demands a thickness of 1  $\mu\text{m}$ . Such requirement demands nanosized dielectric powders with uniform composition and size distribution [3-4].  $\text{BaTiO}_3$  is found in many crystalline forms major among them are tetragonal and cubic phase. Tetragonal  $\text{BaTiO}_3$  powder has better sintering behavior, high density, and higher dielectric constants compared to the cu-

bic phase. Traditionally,  $\text{BaTiO}_3$  is prepared by solid state reaction at high temperature of approximately 1200°C, which result high crystallite size, wide grain size distribution, multiple phases, irregular morphologies and consequent poor optimization and reproducibility of electrical properties [5]. For the preparation of nanosized BT particles with high homogeneity, uniform shape and narrow size distribution, wet chemical synthesis methods, including sol-gel [6], microemulsion [7], hydrothermal synthesis [8-9] and polymeric precursors method [10-12] have been used. The oxalate precursor route is the most intensely examined route for generation  $\text{BaTiO}_3$  from complex precursor. The use of an inexpensive inorganic salt precursor improves the cost-effectiveness of the powder production which facilitates synthesis of the crystallized powder with ultrafine particle size and high purity [13]. From our knowledge, there is no data in the literature for synthesis of  $\text{BaTiO}_3$  by oxalate precursor method using titanium dioxide as raw materials. In addition, there is also no information about the optimum conditions for synthesis of the BT nanopowders through oxalate precursor method. In the present work, not only the oxalate precursor method for preparation of nanocrystalline BT powders using commercial materials, *e.g.*, titanium di-

\*corresponding author. E-mail: rashad133@yahoo.com

oxide and barium chloride, was investigated, but also the application of the statistically designed experiments (Box-Behnken method) have been used to determine the optimum conditions of the significant parameters (*i.e.*, calcination temperature, calcination time, and oxalic acid mole ratio at Ba:Ti mole ratio equal to 1). The obtained BT powders were characterized by XRD and SEM.

## Experimental

BaTiO<sub>3</sub> powder was prepared following the oxalate precursor method using barium chloride BaCl<sub>2</sub>·2H<sub>2</sub>O (98.6%, BDH Chemical Ltd.), titanium dioxide TiO<sub>2</sub> (Fluka > 99.8% purity) and oxalic acid as source of organic acid [El-Nasr Pharmaceutical Chemical Co., Egypt > 99.5%]. For preparation of BaTiO<sub>3</sub> powders using oxalate precursor method, an experimental design, Box-Behnken design [14-15] was used to study the effect of three different studied variables (calcination temperature, calcination time, and oxalic acid mole ratio) on crystal structure, crystallite size and the morphology. The design – matrix of different runs, 15 experiments, as well as the level of each factor are shown in Table 1.

According to this design, the optimal conditions were estimated using a second order polynomial function by which a correlation between studied factors and response (conversion of BaTiO<sub>3</sub> powders %) was generated. The general form of this equation is:

$$E(y) = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} x_i x_j + \sum_{i=1}^3 \beta_{ii} x_i^2 \quad (1)$$

where  $y$  is the estimate of the response variable  $x_i$ 's are the independent variables (calcination temperature, calcination time and oxalic acid mole ratio) that are known for each experimental run, and  $\beta_0$ ,  $\beta_i$ , and  $\beta_{ij}$  are the regression coefficients. The quality of fit of the polynomial was expressed by the coefficient of determination  $R^2$ . Software package, Design Expert 6.1, Stat-Ease, Inc., Minneapolis, USA, was used for regression analysis of experimental data and to plot response surface. Analysis of variance (ANOVA) was used to estimate the statistical parameters. F-test was used to estimate the significant of all terms in the polynomial equation within 95% confidence interval. Figure 1 shows the schematic process diagram

**Table 1**

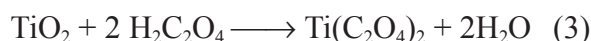
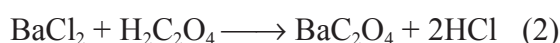
Box-Behnken design with the 3 levels and 3 variables

Run No	Coded Factor Levels		
	Temperature	Time	Oxalic acid mole ratio
1	-1	-1	0
2	+1	-1	0
3	-1	+1	0
4	+1	+1	0
5	-1	0	-1
6	+1	0	-1
7	-1	0	+1
8	+1	0	+1
9	0	-1	-1
10	0	+1	-1
11	0	-1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0

Factors and levels for experimental design using Box-Behnken method

Variables	-1	0	+1
Temperature, °C	800	1000	1200
Time, h	0.5	2.25	4
Oxalic acid mole ratio	0.5	1	1.5

for synthesis of BT nanopowders. Aqueous solution of BaCl<sub>2</sub> and TiO<sub>2</sub> were prepared then; certain amount of oxalic acid related to stoichiometry ratios of Ba<sup>+2</sup> and Ti<sup>+4</sup> was added to the solution according to the following equations:



The oxalic acid mole ratio related to both two reactions is 1. The solution was stirred and evaporated at 80°C until dried. The dry precursors formed were calcined at a rate of 10 °C/min in static air atmo-

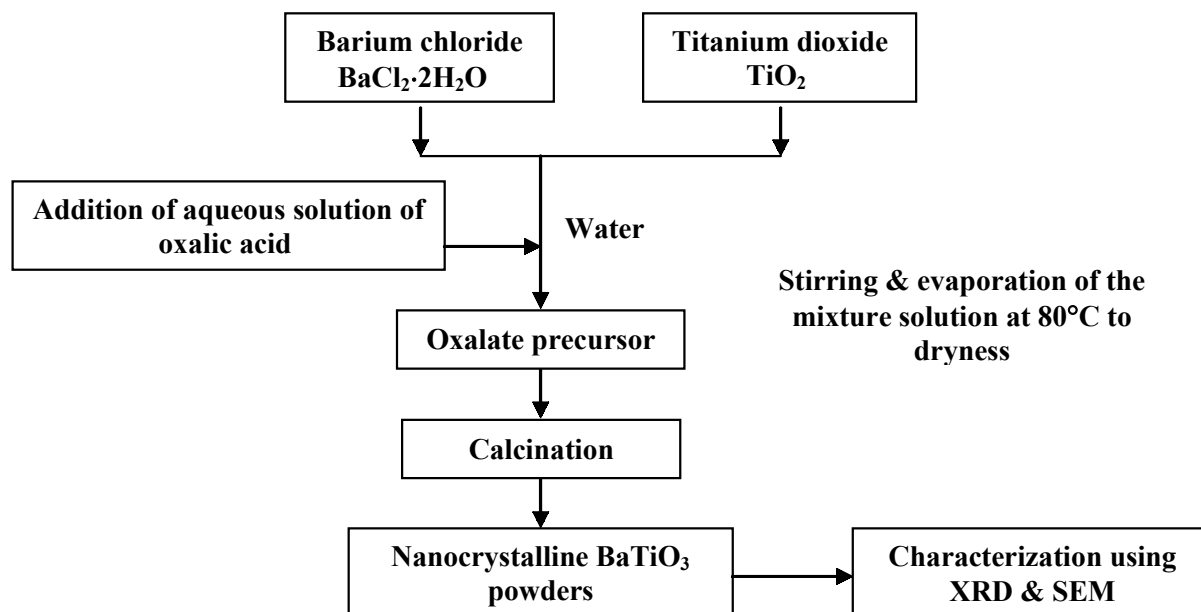


Fig. 1. Schematic flow chart of oxalate precursor method.

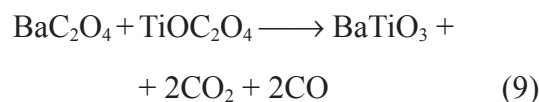
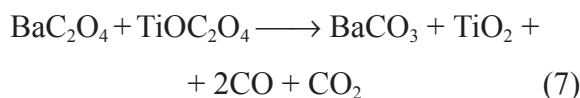
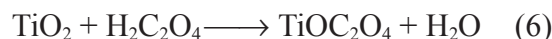
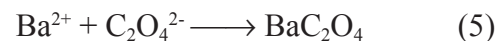
sphere up to different temperatures (800-1200°C) at different time from 0.5-4 hrs. The final products were characterized using X-ray diffraction (XRD) on a Bruker axis D8 diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.504 \text{ \AA}$ ). The average crystallite size of the powders was estimated automatically from corresponding XRD data using X-ray line-broadening technique employing the classical Debye-Scherrer formula for the most intense peak (110) plane determined from the X-ray diffraction data according to the following equation:

$$d_{RX} = k\lambda/\beta\cos\theta \quad (4)$$

where  $d_{RX}$  is the crystallite size,  $k = 0.9$  is a correction factor to account for particle shapes,  $\beta$  is the full width at half maximum (FWHM) of the most intense diffraction peak (110) plane,  $\lambda$  is the wavelength of Cu target = 1.5406 Å, and  $\theta$  is the Bragg angle. The particles morphologies were observed by scanning electron microscopy (JEOL, JSM-5400).

## Result and Discussion

In oxalate precursor, the barium titanate powders were formed by transformation of barium chloride and titanium dioxide in the presence of oxalic acid into barium titanyl oxalate ( $\text{BaC}_2\text{O}_4$ ,  $\text{TiOC}_2\text{O}_4$ ) precursor. The formed precursors were converted to barium titanate by heating at different temperatures according to the following equations [10]:



The effect of three variables on the synthesis of  $\text{BaTiO}_3$  nanopowders studied were calcination temperature (800-1200°C), calcination time (0.5-4 hrs), and oxalic acid mole ratio related to added ratio of barium and titanium (0.5-1.5). The conversion % of the  $\text{BaTiO}_3$  and the crystallite size at different conditions were listed in Table 2. The conversion % of barium titanate was estimated qualitatively from XRD results using the relationship:

$$\text{Conversion} = \frac{I_1}{I_1 + I_2 + I_3} \times 100\% \quad (10)$$

where  $I_1$ ,  $I_2$  and  $I_3$  are the intensities of the main peaks of various phases.

Figure 2 shows the effect of calcination temperature and calcination time on conversion % of produced tetragonal  $\text{BaTiO}_3$  at different oxalic acid mole ratios taking into account that BT powder are of tetragonal phase.

**Table 2**

Experimental Box Behnken Design with the 3 levels and 3 variables utilized in the experiment with the BaTiO<sub>3</sub> conversion (%) and crystallite size (nm)

Exp.	Temperature, °C	Time, hrs	Oxalic acid mole ratio	Crystallite size, nm	BaTiO <sub>3</sub> conversion, %
1	800	0.5	1	63	15.8
2	1200	0.5	1	82.7	95.1
3	800	4	1	55.5	80
4	1200	4	1	87.6	100
5	800	2.25	0.5	68.4	100
6	1200	2.25	0.5	92.7	100
7	800	2.25	1.5	41.6	73.2
8	1200	2.25	1.5	96	95.7
9	1000	0.5	0.5	70	95.45
10	1000	4	0.5	73.7	90.32
11	1000	0.5	1.5	44.8	52.5
12	1000	4	1.5	56.8	77
13	1000	2.25	1	69	100
14	1000	2.25	1	73.2	100
15	1000	2.25	1	70.1	100

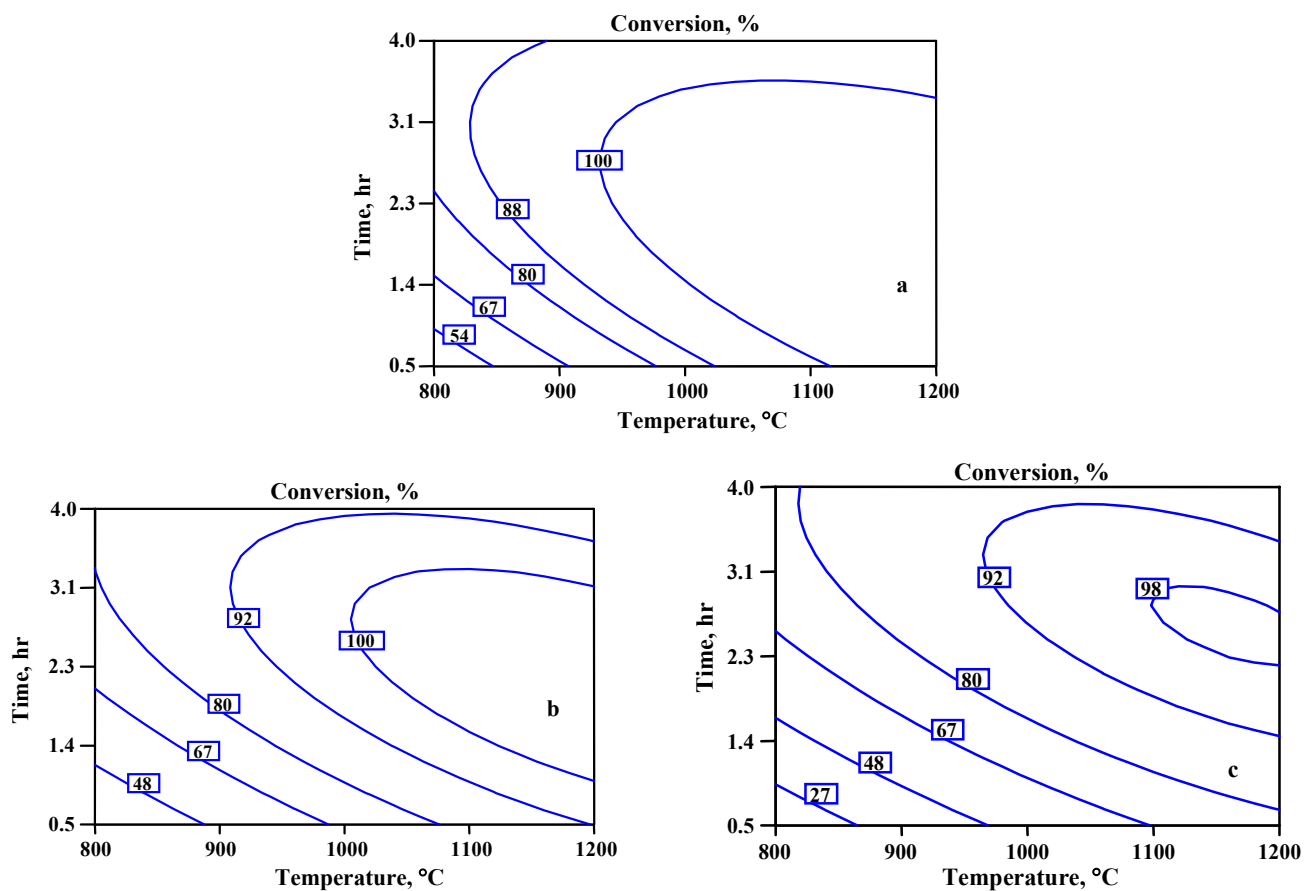


Fig. 2. Effect of calcination temperature and calcination time on conversion % of BaTiO<sub>3</sub> at different oxalic acid mole ratio.

X-ray diffraction (Fig. 3) and SEM (Fig. 5) results confirm the crystallinity, phase structure and the morphology of the produced BaTiO<sub>3</sub> powders. From Table 2 and Figure 2, the results showed that at oxalic acid mole ratio 0.5, a pure well crystallite single phase of tetragonal barium titanate was obtained at different temperatures from 800-1200°C (Run 5 and 6). The average crystallite size was increased by increasing the temperature. It was increased from 68.4 nm at low calcination temperature 800°C to 92.7 nm at high calcination temperature 1200°C. By increasing the oxalic acid mole ratio to 1, the single phase of barium titanate was formed at high temperature from 800-1200°C and calcination time from 2.25 to 4 hrs (Run 4, 13, 14 and 15).

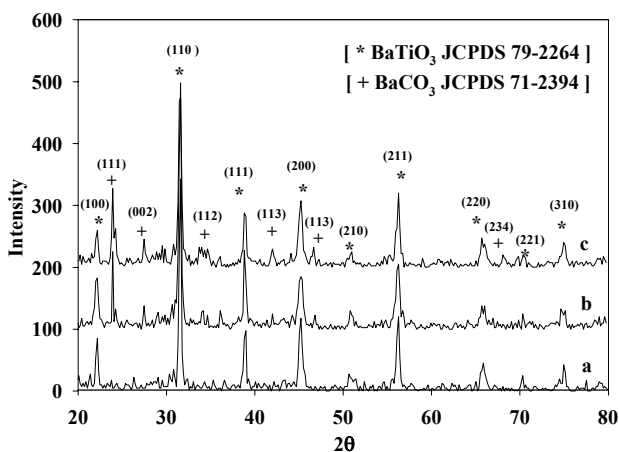


Fig. 3. XRD analysis of the product barium titanate using oxalic acid.

The average crystallite size (Table 2) of the powder was in the range between 69-87.6 nm. At low temperature, the conversion of oxalate precursors into barium titanate powders was decreased. Two phases of tetragonal barium titanate and BaCO<sub>3</sub> were formed. the conversion % of barium titanate was increased from 15.8% to 80% by increasing the calcination time from 0.5 hr to 4 hrs at 800°C (Run 1, 2). By increasing the calcination temperature to 1200°C at low calcination time 0.5 hr, the conversion % of barium titanate was 95.1% (Run 3). With increasing the oxalic acid mole ratio to 1.5, no single phase of tetragonal barium titanate was formed at different studied temperature and time. The conversion % of the obtained barium titanate nanopowders was in the range between 52.5-95.7% (Run 7, 8, 11, and 12).

Figure 3 showed the XRD pattern of the produced tetragonal phase BaTiO<sub>3</sub> at different oxalic acid mole

ratios and temperature 800°C and calcination time 2.25 hrs. From the XRD data, it is noticed that at oxalic acid mole ratio 0.5, a single phase of tetragonal BaTiO<sub>3</sub> was obtained (JCPDS #79-2264). The diffraction peaks corresponded to the strongest diffraction planes (110), (111), (200), and (211) at 2θ values of 31.508°, 38.876°, 45.236°, 56.209° which ascribed to tetragonal BaTiO<sub>3</sub> were obtained. By increasing the oxalic acid mole ratios to 1 and 1.5, a mixture of tetragonal BaTiO<sub>3</sub> and barium carbonate BaCO<sub>3</sub> (JCPDS #71-2394) were formed, the diffraction peaks corresponded to the strongest diffraction planes (111), (002), (112), (221) at 2θ values of 23.894°, 27.501°, 34.118°, 41.963° related to BaCO<sub>3</sub> were obtained. Increasing the oxalic acid mole ratio increases the calcination temperature and calcination time until the precursor converted to BaTiO<sub>3</sub> while decreasing the oxalic acid mole ratio was decreases the temperature and then increased the conversion of the precursor to BaTiO<sub>3</sub> nanopowders. It is worth to mention that organic acid precursor method is a successful and low cost method for preparation of barium titanate nanopowders since in our study; it depends on the commercial chemical such as TiO<sub>2</sub>, BaCl<sub>2</sub> and oxalic acid which are available and this is the first time created to correlate the relationship between the three variables (calcination time, calcination temperature and oxalic acid mole ratio) on the BT conversion % and crystallite size. In similar studies, Vinothini *et al.* [8] used citric acid as organic acid precursor for synthesis of tetragonal barium titanate nanopowders using barium carbonate and titanium isopropoxide as the sources of barium and titanium, respectively at Ba:Ti mole ratio 1 and they showed that the complete transformation of the produced precursors into tetragonal BaTiO<sub>3</sub> phase was finally achieved after annealing time 8 hrs and annealing temperature 900°C. Potdar *et al.* [10] used oxalic acid as organic acid precursor and butyl titanate as a source of titanium and barium acetate as a source of barium and they indicated that a single phase of pure tetragonal BT was formed at annealing temperature 1160°C for 5 hrs. Hwu *et al.* [16] used barium chloride and titanium tetrachloride with oxalic acid mole ratio 2.2 and the formed BT single phase was obtained at 800°C for 6 hrs. Moreover, Ghosh *et al.* [17] synthesized barium titanate using barium nitrate and titanyl nitrate in the presence of tartaric acid as organic acid precursor and the conversion of the formed precursor to get tetragonal BT with 90% yield.

All the experimental results, collected in the 3-D cubic as shown in Fig. 4, revealed that the conversion % of barium titanate, ranging from 11% to 100%, were achieved. The smallest conversion of BT can be obtained at low levels of calcination temperature and calcination time and high level of oxalic acid mole ratio. The formation of  $\text{BaTiO}_3$  with conversion percentage of 11.75% can be obtained at low calcination temperature and low calcination time. On the other hand, the formation of pure  $\text{BaTiO}_3$  100%, can be achieved at high level of calcination temperature and low levels of both calcination time and oxalic acid mole ratio. The average crystallite size from 3-D cubic graph showed that the lowest crystallite size can be obtained at low levels of calcination temperature and calcination time and high level of oxalic acid mole ratio. In contrast, the highest crystallite size can be obtained at high levels of calcination time, calcination temperature and oxalic acid mole ratios.

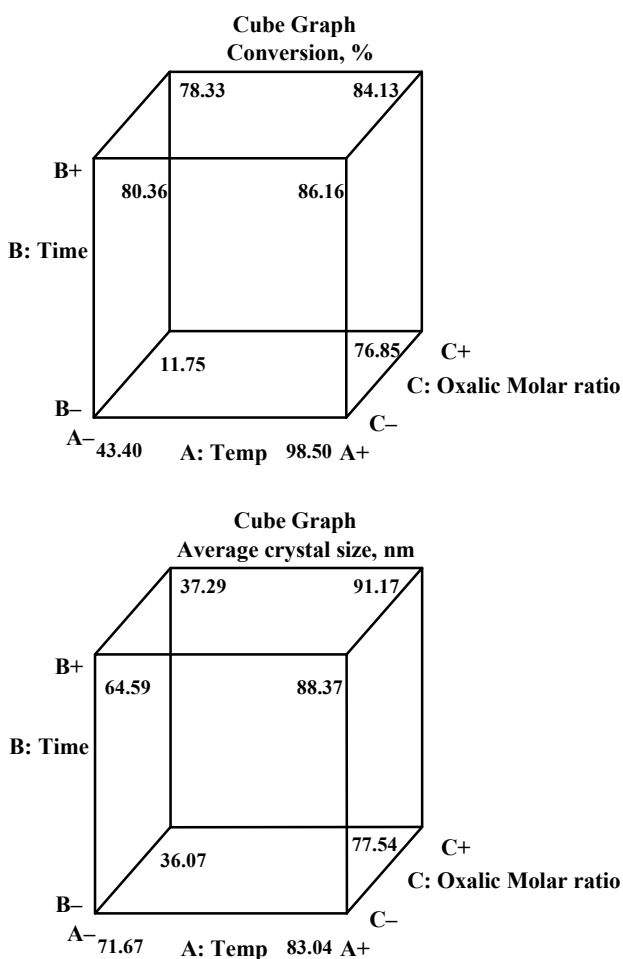


Fig. 4. Cubic graphs for conversion of the precursors to  $\text{BaTiO}_3$  nanopowders and average crystallite size of the produced powders in studied region.

SEM micrographs of the formed  $\text{BaTiO}_3$  nanopowders at different oxalic acid mole ratios and low calcination temperature  $800^\circ\text{C}$  are given in Fig. 5. A pure single tetragonal structure shape can be obtained at low oxalic acid mole ratio. The formed BT particles were homogenous, very fine and the crystallite size was identical to the data obtained from XRD. The tetragonal structure obtained,  $\text{BaTiO}_3$  without any agglomeration of small crystal size. Increasing the oxalic acid mole ratio up to 1, mixture of two shapes (tetragonal and orthorhombic shapes) with random particle size distribution was obtained.

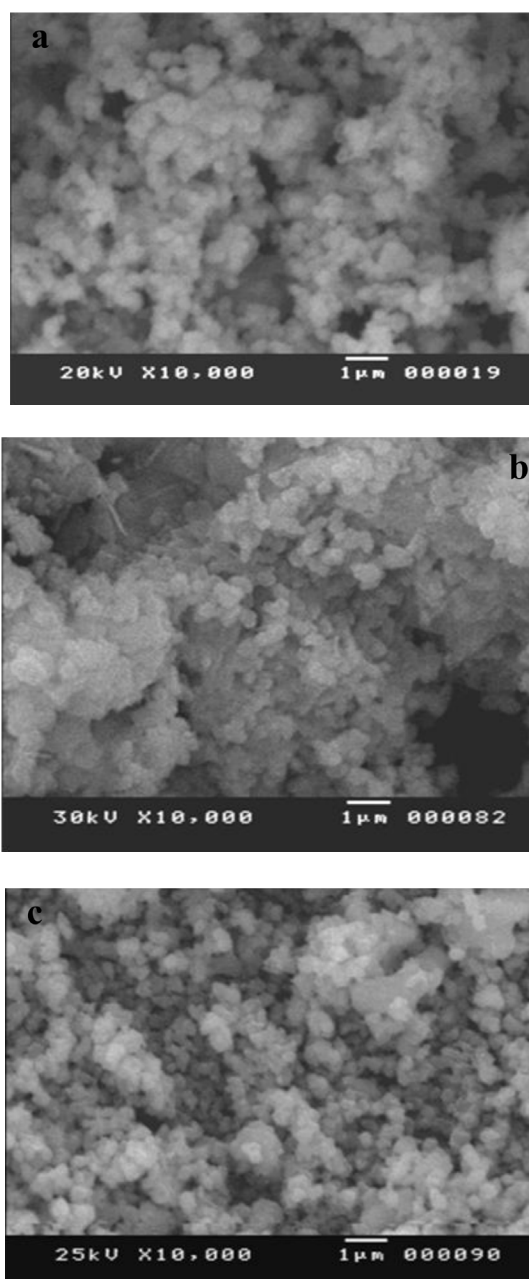


Fig. 5. SEM micrographs of barium titanate nanopowders.

## Conclusions

Barium titanate nanoparticles have been synthesized through oxalate acid precursor. Effects of three variables of calcination temperature, calcinations time, and oxalic acid mole ratio on the crystal structure, crystallite size and morphology of BaTiO<sub>3</sub> nanopowders were studied. A well crystalline single phase tetragonal barium titanate powders was obtained at low oxalic acid ratios from 0.5 to 1 at different temperatures from 800 to 1200°C and calcination time from 2.25-4 hrs. The smallest crystallite size (36 nm) can be obtained crystallite size at low levels of calcination temperature (800°C) and calcination time (0.5 hr) and high level of oxalic acid mole ratio (1.5). In contrast, the highest crystallite size (91 nm) can be obtained high levels of calcination time (4 hrs), calcination temperature (1200°C) and oxalic acid mole ratio (1.5). The crystalline size of obtained BaTiO<sub>3</sub> nanopowders was ranged from 36 to 91 nm. SEM micrographs showed that the produced pure BT nanopowders were formed in the tetragonal structure shape.

## References

1. Xing, X., Deng, J., Chen, J., Liui, G., J. Alloys compd. 384:312 (2004).
2. Cho, J. H., Kuwabara, M., J. Eur. Ceram. Soc. 24:2959 (2004).
3. Venigalla, S., Am. Ceram. Soc. Bull. 6:45 (1999).
4. Zhu, W., Akbar, S.A., Asiaie, R., Dutta, P.K., J. Appl. Phys. 36:214 (1997).
5. Eckert, J.O., Houston, C.C.H., Gersten, B.L., Lencka, M.M., Riman, R.E., J. Am. Ceram. Soc. 79:2929 (1996).
6. Hernandez, B.A., Chang, K., Fisher, E.R., Dohrout, P.K., Chem. Mater. 14:480 (2002).
7. Wang, J., Fang, J., Gan, L.M., Chew, C.H., Wang, X., Shen, Z., J. Am. Ceram. Soc. 82:873 (1999).
8. Vinothini, V., Singh, P., Balasubramanian, M. Ceram. Int. 32:99 (2006).
9. Kang, L.B., Zhang, R.F., Que, W.X., J. Alloys Compd. 337:226 (2002).
10. Potdar, H.S., Deshpande, S.B., Date, S.K., Mater. Chem. and Phys. 58:121(1999).
11. Potdar, H.S., Deshpande, S.B., Date, S.K., J. Am. Ceram. Soc. 79:2795 (1996).
12. Kholam, Y.B., Deshpande, A.S., Potdar, H.S., Deshpande, S.B., Date, S.K., Patil, A.J., Mater. Lett. 55:175 (2002).
13. Seveyrat, L.S, Hajjaji, A., Emziane, Y., Guiffard, B., Guyomar, D., Ceramic International 33:35 (2007).
14. Cornell, J.A., Ontgomery, D.C., Qual. J., Technol. 28:163 (1996).
15. Abdel-Aal, E.A., Malekzadeh, S.M., Rashad, M.M., EL-Midany, A.A., EL-Shall, H., Powder Technol. 171:63 (2006).
16. Hwu, J.-M., Yu, W.-H., Yang, W.-C., Chen, Y.-W., Chou, Y.-Y., Mater. Res. Bull. 40:1662 (2005).
17. Ghosh, S., Dasgupta, S., Sen, A, Maiti, H.S., Mater.Lett.61:538 (2007).

*Received 13 February 2007.*