Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 669–672
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Formation mechanism of barium titanate by thermal decomposition of barium titanyl oxalate

Won-Sik Jung [a], Bong-Ki Min [b], Jiho Park [c], Dang-Hyok Yoon [a,*]

[a] *School of Materials Science and Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea*
[b] *Instrumental Analysis Center, Yeungnam University, Gyeongsan 712-749, Republic of Korea*
[c] *Nano Materials Team, Samsung Fine Chemicals Co., Ltd., Daejeon 305-380, Republic of Korea*

Received 19 July 2010; received in revised form 27 July 2010; accepted 24 September 2010
Available online 29 October 2010

Abstract

This study examined the formation mechanism of $BaTiO_3$ from the thermal decomposition of barium titanyl oxalate. A significant amount of O_2 evolution near 357 and 720 °C was observed by gas chromatography/mass spectroscopy, except for the previously known H_2O, CO_2, CO evolution. The metastable $Ba_2Ti_2O_5CO_3(CO_2)$ intermediate phase seemed to be transformed mainly to $Ba_2Ti_2O_5CO_3$, while a certain amount of crystalline $BaCO_3$ and amorphous Ti-rich phase were formed simultaneously at 450–600 °C in air. A modification of the decomposition mechanism reported by Gopalakrishnamurthy et al. was proposed based on the experimental findings.

Keywords: $BaTiO_3$; Oxalate method; Thermal decomposition; Mechanism

1. Introduction

Barium titanate ($BaTiO_3$) is one of the most widely used ceramic materials in industry owing to its excellent dielectric properties. The increasing trend for miniaturization in the electronics industry has created a strong demand for nano-sized $BaTiO_3$ with a spherical shape, low sintering temperature with a high sintering density, and high dielectric constant with a low dissipation factor. Among many kinds of $BaTiO_3$ synthetic methods, the oxalate method is known to produce finer particles with better homogeneity, higher purity and lower processing temperatures over the conventional solid-state reacted powder. The oxalate route co-precipitates barium titanyl oxalate tetrahydrate (BTO: $BaTiO(C_2O_4)_2{\cdot}4H_2O$) as a precursor for $BaTiO_3$, according to Eq. (1):

$$BaCl_2{\cdot}2H_2O + TiOCl_2 + 2H_2C_2O_4{\cdot}2H_2O \rightarrow BaTiO(C_2O_4)_2{\cdot}4H_2O + 4HCl \quad (1)$$

$BaTiO_3$ particles can be obtained by the successive thermal decomposition of BTO at >750 °C.

Since Clabaugh et al. reported the thermo-analytical results on BTO decomposition in 1956 [1], much effort has been made to explain the $BaTiO_3$ formation mechanism from BTO. However, there are some controversies regarding the thermal decomposition mechanism of BTO because no intermediate phases could be defined clearly. Due to the existence of amorphous phases up to 600 °C, most of the intermediate phases can only be estimated through indirect experimental results, such as thermal behavior, FT-IR and Raman spectra [2–6]. An example is the appearance of $BaCO_3$ and TiO_2 as intermediate phases, where some researchers proposed the formation of these as intermediate phases [2,4,6,7–13], while others denied [1,3,14–16]. Although there are some reports on the decomposition mechanism of BTO [3,6,7,9,10,13–16], the model proposed by Gopalakrishnamurthy et al. in 1975 is generally accepted [3], which can be divided into the following 5 steps:

Step 1: Dehydration of BTO

$$BaTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{RT-180^\circ C} BaTiO(C_2O_4)_2 + 4H_2O \quad (2)$$

Step 2: Initial low temperature decomposition of BTO

$$2BaTiO(C_2O_4)_2 \xrightarrow{180-250^\circ C} Ba_2Ti_2O_2(C_2O_4)_3CO_3 + CO \quad (3)$$

---

* Corresponding author. Tel.: +82 538102561; fax: +82 538104628.
E-mail address: dhyoon@ynu.ac.kr (D.-H. Yoon).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.09.056

Step 3: Main decomposition of BTO

$$Ba_2Ti_2O_2(C_2O_4)_3\,CO_3 \xrightarrow{250-450^\circ C} Ba_2Ti_2O_5CO_3(CO_2) + 2CO_2 + 3CO \tag{4}$$

Step 4: Evolution of entrapped CO_2

$$Ba_2Ti_2O_5CO_3(CO_2) \xrightarrow{450-600^\circ C} Ba_2Ti_2O_5CO_3 + CO_2 \tag{5}$$

Step 5: Final decomposition of carbonate and the formation of $BaTiO_3$

$$Ba_2Ti_2O_5CO_3 \xrightarrow{600-750^\circ C} 2BaTiO_3 + CO_2 \tag{6}$$

A modification of the above BTO decomposition mechanism will be proposed in this paper to explain the new findings observed during oxalate process for $BaTiO_3$ synthesis.

2. Experimental procedure

Barium titanyl oxalate (BTO) was offered by Samsung Fine Chemicals Co., LTD. The Ba/Ti molar ratio after calcination was 1.000. Thermal decomposition behavior of BTO was examined by theremogravimetry/differential thermal analysis (TG/DTA: SDT Q600, TA Instruments, USA) in a flowing air atmosphere from room temperature to 1000 °C at a heating rate of 5 °C/min. High temperature X-ray diffraction (HT-XRD: D/MAX-RB, Rigaku using Cu K_α line, 40 kV and 300 mA) was performed for BTO from 300 to 900 °C in every 100 °C step after holding for 3 min at each measurement temperature to confirm in situ the phases generated during heat treatment. The evolved gases, such as H_2O, CO, CO_2 and O_2, during the BTO decomposition were analyzed by gas chromatography/mass spectroscopy (GC/MS: 6890N/5975 iMS, Agilent, USA) at the temperature range of 100–800 °C in a flowing He atmosphere.

3. Results and discussion

TG/DTA results are shown in Fig. 1, which are divided into 5 different temperature regions, according to Gopalakrishnamurthy et al.'s model. The depth of the DTA endothermic peak and TG weight loss by dehydration at step 1 would depend on the amount of adsorbed water. After a small weight loss by the initial low temperature BTO decomposition at step 2, an abrupt weight loss occurred at step 3 by the main decomposition of BTO showing an exothermic DTA peak. Approximately 40% of the total weight loss of BTO occurs at this step, which involves the evolution of gases, such as CO and CO_2. Entrapped CO_2 is evolved at step 4 followed by the final endothermic decomposition of carbonate and the formation of $BaTiO_3$ at step 5.

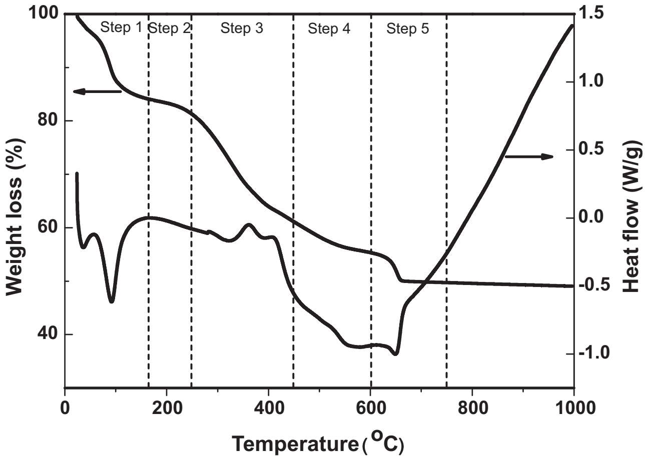

Fig. 1. TG/DTA behavior of BTO between room temperature to 1000 °C in air.

HT-XRD patterns up to 900 °C are shown in Fig. 2, which was performed to examine the phase formation in real time, including the existence of $BaCO_3$ and TiO_2. According to Fig. 2(a), the BTO peaks disappeared at temperatures >300 °C, and only amorphous phases were observed at the temperature range of 300–500 °C. After partial crystallization of an intermediate phase at 600 °C, $BaTiO_3$ was found to be the main phase from 700 °C. With an enlarged HT-XRD pattern

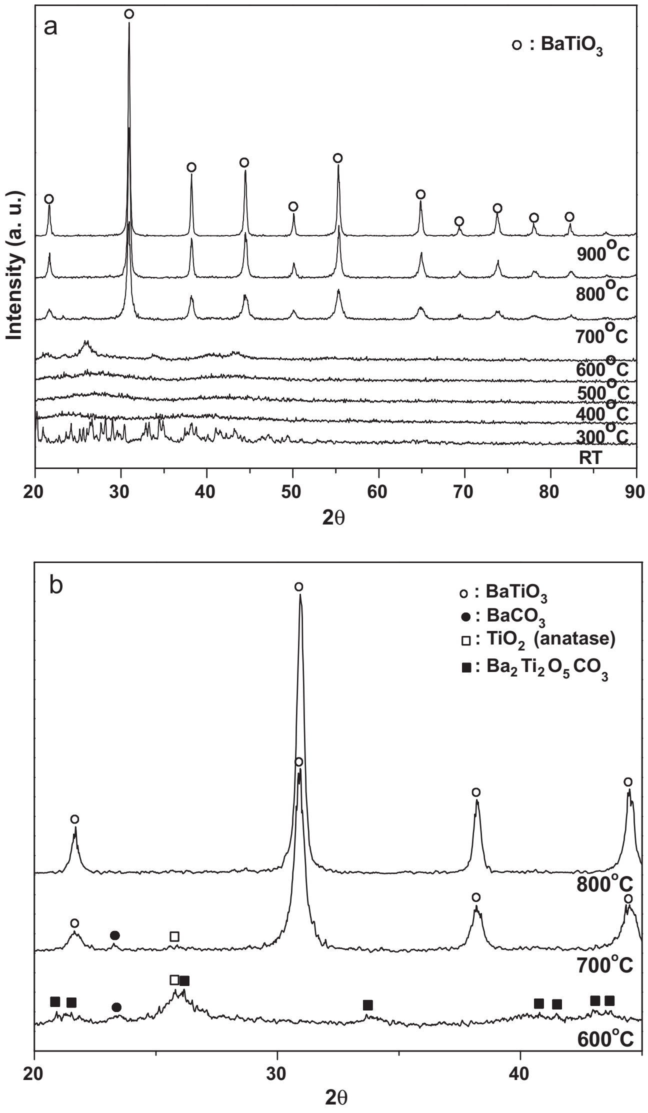

Fig. 2. (a) HT-XRD patterns showing the evolution of phases from BTO in air from room temperature to 900 °C and (b) the enlarged patterns with the indices of the phases present.

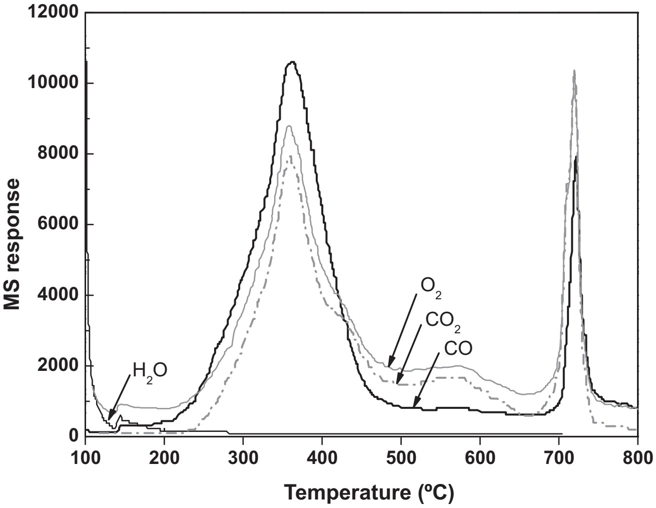

Fig. 3. GC/MS spectra of the gases evolved during the thermal decomposition of BTO.

shown in Fig. 2(b), the characteristic peaks of $BaCO_3$ and anatase TiO_2 were observed at 600 and 700 °C, even though the peak height was small. The other peaks at 600 °C were assigned to a barium titanium oxycarbonate ($Ba_2Ti_2O_5CO_3$) phase, which was proposed for the first time by Gopalakrishnamurthy et al. [3] and confirmed to be a highly disordered, metastable and weak crystalline phase by Kumar et al. [4]. Although most of the intermediate phases had transformed into $BaTiO_3$ at 700 °C, a small amount of $BaCO_3$ and TiO_2 were still present. Pure $BaTiO_3$ is expected from >700 °C according to the HT-XRD results, which is consistent with the TG results, showing weight loss up to 720 °C, in Fig. 1.

Fig. 3 shows the gases evolved during the thermal decomposition of BTO measured by GC/MS. The evolution of water vapor was observed mainly to 180 °C. The main evolutions of CO and CO_2 occurred at 357 and 720 °C, which are similar to the findings reported by Xu et al. [6]. The gaseous evolution at 357 °C and CO_2 evolution at 720 °C can be explained by Eqs. (4) and (6), respectively. However, it is unclear why CO is evolved at 720 °C, which cannot be explained by Eq. (6). According to the GC/MS spectra shown in Fig. 3, significant amount of O_2 was evolved at 357 and 720 °C, which is opposed to the general belief so far that CO, CO_2 and H_2O are the only gaseous products of BTO decomposition [3,6,7,9,10,13–16].

The coexistence of CO, O_2 and CO_2 seems to be possible. According to the free energy (ΔG) calculation for the formation of CO_2 from CO and O_2 ($CO + 1/2O_2 = CO_2$) at an equilibrium condition, ΔG indicates a high driving force for this reaction, i.e., −228 and −187 kJ for a mole of CO_2 formation at 357 and 720 °C, respectively. However, this reaction does not seem to occur rapidly due to the kinetic matter. Actually, many researchers [17–25] have tried to enhance CO_2 conversion rate from CO and O_2 up to 1000 K using various kinds of catalysts, which explains the possibility of the coexistence of CO, O_2 and CO_2. Lian et al. [24] reported that the CO_2 oxidation rate depended significantly on the type of catalysts, showing the conversion rate of 0–94.8% at a dry condition. Wang and Zhong [25] explained the coexistence of CO, O_2 and CO_2 using a high activation energy of ≈50 kJ/mol for the dissociation of O_2 for the above temperature ranges, which is the rate-determining step for CO oxidation.

These observations, such as the evolution of O_2 near 357 and 720 °C, CO evolution near 720 °C, and the existence of $BaCO_3$ and TiO_2 at 600–700 °C, suggest that the reaction mechanism by Gopalakrishnamurthy et al. [3] needs to be modified in the following 3 aspects. In order to explain the evolution of O_2 near 357 °C, Eq. (4) needs to be modified at step 3:

$$Ba_2Ti_2O_2(C_2O_4)_3\,CO_3 \xrightarrow{250-450^\circ C} Ba_2Ti_2O_5CO_3(CO_2) + 2(1-x)CO_2 + (3+2x)CO + xO_2 \tag{4-1}$$

The second is the modification of equation (5) to explain the existence of a small amount of $BaCO_3$ and TiO_2 at 450–600 °C at step 4:

$$Ba_2Ti_2O_5CO_3(CO_2) \xrightarrow{450-600^\circ C} (1-x)Ba_2Ti_2O_5CO_3 + (1-x)CO_2 + 2xBaCO_3 + 2xTiO_2 \tag{5-1}$$

The third is the modification of Eq. (6) to explain the evolution of CO and O_2 gases near 720 °C and the addition of $BaTiO_3$ formation from $BaCO_3$ and TiO_2 at step 5 using the following 2 equations:

$$Ba_2Ti_2O_5CO_3 \xrightarrow{600-750^\circ C} 2BaTiO_3 + (1-x)CO_2 + xCO + x/2O_2 \tag{6-1}$$

$$BaCO_3 + TiO_2 \xrightarrow{600-750^\circ C} BaTiO_3 + CO_2 \tag{6-2}$$

Table 1 lists the weight losses between the observed and calculated values for 5 BTO decomposition steps. Both values are similar except for a 1.7 wt.% difference for the final $BaTiO_3$

Table 1
Comparison of the weight loss between the theoretical and observed values for 5 thermal decomposition steps of BTO.

Decomposition step	Temperature range (°C)	Calculated weight loss (wt.%)	Observed weight loss (wt.%)
Dehydration of BTO	RT–180	16.04	16.26
Low temperature decomposition of BTO	180–250	3.12	2.72
Main decomposition of BTO	250–450	19.14	19.82
Evolution of CO_2	450–600	4.90	4.85
$BaTiO_3$ formation	650–750	4.90	6.61
Total	RT–750	48.10	50.26

formation at step 5, where the observed value is larger than the calculated one. The additional weight loss at step 5 may be due to the evolution of CO_2 when $BaTiO_3$ is formed from $BaCO_3$ and TiO_2 according to Eq. (6-2), which is in contrast to the theoretical base of Eq. (6) used for the calculation.

4. Conclusions

The mechanism for the formation of $BaTiO_3$ from the thermal decomposition of barium titanyl oxalate was examined in this study. The formation of $BaCO_3$ and TiO_2 from an intermediate phase of $Ba_2Ti_2O_5CO_3(CO_2)$ at temperatures between 450 and 600 °C was confirmed by high temperature X-ray diffraction. A significant amount of O_2 evolution near 357 and 720 °C was observed by gas chromatography/mass spectroscopy, except for H_2O, CO_2 and CO. A modification of the mechanism reported by Gopalakrishnamurthy et al. was proposed based on these findings.

Acknowledgements

This study was supported by Samsung Fine Chemicals Co., Ltd. We would like to thank Nano Materials Team at Samsung Fine Chemicals Co., for BTO preparation and helpful discussions.

References

[1] W.S. Clabaugh, E.M. Swiggard, R. Gilchrist, Preparation of barium titanyl oxalate tetrahydrate for conversion to barium titanate of high purity, J. Res. Natl. Bur. Stds. 56 (1956) 289–291.

[2] P.K. Gallagher, J. Thomson Jr., Thermal analysis of some barium and strontium titanyl oxalates, J. Am. Ceram. Soc. 48 (1965) 644–647.

[3] H.S. Gopalakrishnamurthy, M.S. Rao, T.R.N. Kutty, Thermal decomposition of titanyl oxalates—I. Barium titanyl oxalate, J. Inorg. Nucl. Chem. 37 (1975) 891–898.

[4] S. Kumar, G.L. Messing, W.B. White, Metal organic resin derived barium titanate: I, Formation of barium titanium oxycarbonate intermediate, J. Am. Ceram. Soc. 76 (1993) 617–624.

[5] M. Arima, M. Kakihana, Y. Nakamura, M. Yashima, M. Yoshimura, Polymerized complex route to barium titanate powders using barium–titanium mixed-metal citric acid complex, J. Am. Ceram. Soc. 79 (1996) 2847–2856.

[6] J. Xu, S. Tsutai, S. Hayashi, M. Sugai, Z. Nakagawa, Thermal decomposition process of barium titanyl oxalate tetrahydrate, J. Ceram. Soc. Jpn. 107 (1999) 27–30.

[7] M. Stokenhuber, H. Mayer, J.A. Lercher, Preparation of barium titanates from oxalates, J. Am. Ceram. Soc. 76 (1993) 1185–1190.

[8] O.O. Vasyl'kiv, A.V. Ragulya, V.P. Klimenko, V.V. Skorokhod, Synthesis and sintering of nanocrystalline barium titanate powder under nonisothermal conditions. III. Chromatographic analysis of barium titanyl-oxalate gaseous decomposition products, Powder Metall. Met. C 36 (1997) 575–578.

[9] H.S. Potdar, S.B. Deshpande, S.K. Date, Chemical coprecipitation of mixed (Ba + Ti) oxalates precursor leading to $BaTiO_3$ powders, Mater. Chem. Phys. 58 (1999) 121–127.

[10] A.V. Prasadarao, M. Suresh, S. Komarneni, pH dependent coprecipitated oxalate precursors—a thermal study of barium titanate, Mater. Lett. 39 (1999) 359–363.

[11] A.V. Polotai, A.V. Ragulya, T.V. Tomila, C.A. Randall, The XRD and IR study of the barium titanate nano-powder obtained via oxalate route, Ferroelectrics 298 (2004) 243–251.

[12] V. Ischenko, E. Pippel, R. Köferstein, A.P. Abicht, J. Woltersdorf, Barium titanate via thermal decomposition of Ba, Ti-precursor complexes: the nature of the intermediate phases, Solid State Sci. 9 (2007) 21–26.

[13] V.A. Zazhigalov, V.V. Sidorchuk, S.V. Khalameida, L.S. Kuznetsova, Mechanochemical synthesis of $BaTiO_3$ from barium titanyl oxalate, Inorg. Mater. 44 (2008) 641–645.

[14] S. Otta, S.D. Bhattamisra, Kinetics and mechanism of the thermal decomposition of barium titanyl oxalate, J. Therm. Anal. 41 (1994) 419–433.

[15] H.S. Potdar, S.B. Deshpande, A.S. Desphande, Y.B. Khollam, A.J. Patil, S.D. Pradhan, S.K. Date, Simplified chemical route for the synthesis of barium titanyl oxalate (BTO), Int. J. Inorg. Mater. 3 (2001) 613–623.

[16] Y.S. Malghe, A.V. Gurjar, S.R. Dharwadkar, Synthesis of $BaTiO_3$ powder from barium titanyl oxalate (BTO) precursor employing microwave heating technique, Bull. Mater. Sci. 3 (2004) 217–220.

[17] R.J.H. Voorhoeve, J.P. Remeika, P.E. Freeland, B.T. Matthias, Rare-earth oxides of manganese and cobalt rival platinum for the treatment of carbon monoxide in auto exhaust, Science 177 (1972) 353–354.

[18] H. Falcón, M.J. Martinez-Lope, J.A. Alonso, J.L.G. Fierro, Defect $LaCuO_{3-\delta}$ ($\delta = 0.05$–0.45) perovskites bulk and surface structures and their relevance in CO oxidation, Appl. Catal. B 26 (2000) 131–142.

[19] Y. Zhang-Steenwinkel, J. Beckers, A. Bliek, Surface properties and catalytic performance in CO oxidation of cerium substituted lanthanum–manganese oxides, Appl. Catal. A 235 (2002) 79–92.

[20] J. Zhu, Z. Zhao, D. Xiao, J. Li, X. Yang, Y. Wu, CO oxidation, NO decomposition, and NO + CO reduction over perovskite-like oxides La_2CuO_4 and $La_{2-x}Sr_xCuO_4$: An MS-TPD study, Ind. Eng. Chem. Res. 44 (2005) 4227–4233.

[21] C.S. Yan, W.T. Chuang, A. Chaudhari, S.L. Lee, Lattice model studies of CO oxidation kinetic on oscillation over nano-scaled Pt particle: effect of temperature variation and diffusion, Appl. Surf. Sci. 252 (2005) 784–792.

[22] K. Nakao, S. Ito, K. Tomishige, K. Kunimori, Structure of activated complex of CO_2 formation in a $CO + O_2$ reaction on Pd(1 1 0) and Pd(1 1 1), J. Phys. Chem. B 109 (2005) 17553–17559.

[23] K. Nakao, S. Ito, K. Tomishige, K. Kunimori, Comparative study of CO_2 formation in CO oxidation by O_2, NO and NO_2 on Pd(1 1 0) surface using infrared chemiluminescence, Surf. Sci. 600 (2006) 4221–4227.

[24] H. Lian, M. Jia, W. Pan, Y. Li, W. Zhang, D. Jiang, God-base catalyst supported on carbonate for low-temperature CO oxidation, Catal. Commun. 6 (2005) 47–51.

[25] K. Wang, P. Zhong, A kinetic study of CO oxidation over the perovskite-like oxide $LaSrNiO_4$, J. Serb. Chem. Soc. 75 (2010) 249–258.