Thermal Decomposition Process of Barium Titanyl Oxalate Tetrahydrate

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Thermal decomposition of barium titanyl oxalate tetrahydrate was investigated in air and nitrogen atmospheres, respectively. Decomposition process is divided into four steps; dehydration, decomposition, crystallization and the production of BaTiO3. In air atmosphere, after dehydration and the decomposition of barium titanyl oxalate, a small amount of BaCO3 and TiO2 is formed through the reaction between the decomposition product and the generated CO2 gas in air atmosphere, while the other large part of the decomposition product crystallizes out as intermediate phase (Ba2Ti2O5CO3) in intermediate process of decomposition. In nitrogen atmosphere, however, BaTiO3 is only formed through decomposition of intermediate phase.

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1. Introduction

Conventional solid-state reaction method used for preparing barium titanate (BaTiO3) powders usually involves a mixed-oxide process which first requires mixing TiO2 and BaCO3 using ball-milling and then calcining the resulting mixture at an appropriate temperature. Such processes have well-recognized disadvantages such as compositionally inhomogeneous mixing and impurities which are introduced during milling. Barium titanate has also been prepared by a variety of wet chemical methods, including sol-gel method, thermal decomposition method of oxalate or citrate, and thermal synthesis method, etc. Potential advantages of these wet chemical methods over the conventional solid-state reaction method include better homogeneity, better stoichiometry, higher purity, and lower processing temperature. In thermal decomposition of oxalate (BaTiO3(C2O4)2·4H2O) or citrate (BaTi(C6H6O7)3·6H2O) in these wet chemical methods, two contradictory mechanisms exist. Gallagher and Thomson Jr. proposed that highly reactive BaCO3 and TiO2 were formed prior to the formation of BaTiO3.1) In contrast, some authors denied the appearance of BaCO3 and TiO2 as intermediate phases, and suggested a carbonate complex (Ba2Ti2O5CO3) formed as a final intermediate phase.2)-4)

The conflicting literature reports1)-4) and the inadequate support for either mechanism clearly show that the mechanism of BaTiO3 formation from oxalate or citrate is not well understood. In this study, decomposition process of BaTiO3(C2O4)2·4H2O was studied using X-ray diffractometer (XRD), TG/DTA, IR spectroscopy, and Mass spectrometry. Some new results indicated that not only BaCO3 and TiO2 but also intermediate phase appeared during the decomposition process in air atmosphere, while intermediate phase was only formed in N2 atmosphere.

2. Experimental procedure

2.1 Sample preparation

As starting materials, commercially guaranteed reagents (Wako Pure Chemical Industries, Ltd.), BaCl2·2H2O, TiCl4 and anhydrous oxalic acid, were used. The flow-diagram used for preparing BaTiO3(C2O4)2·4H2O is shown in Fig. 1. The molar ratios of barium and oxalic acid to titanium were 1.05 and 2.20, respectively. Barium titanyl oxalate tetrahydrate was prepared at a reaction temperature of 70°C for reaction time of 4h by the method of Clabaugh et al.5) The product was washed well with distilled water and dried on the filter funnel in air. The XRD pattern of the sample prepared in this manner is shown in Fig. 2. This pattern is in agreement with that of the stoichiometric oxalate (BaTiO3(C2O4)2·4H2O) reported by Kudaka et al.6) The cation ratio in the barium titanyl oxalate tetrahydrate obtained was determined by ICP measurement (Seiko Instruments Inc., SPS7700). The ratio of Ba to Ti is 1.01.

2.2 Analysis methods

Thermal decomposition process of oxalate was ini-
vestigated in air and N₂ atmospheres using thermogravimetric and differential thermal analyses (Seiko Instruments Inc., TG/DTA 320). The effluent gas analysis during decomposition process was performed by Mass spectrometry (Mac Science Co., Ltd., TG-DTA/MS System) in He atmosphere. Measurements of TG/DTA and Mass spectrometry were done at a rate of 10°C/min. The identification of the products generated by decomposition of oxalate fired at various temperatures in the range 100–900°C in air and N₂ for 2 h were performed using X-ray diffractometer (XRD, Rigaku Co., RINT2400) with radiation of Cu Ka (λ=0.154178 nm) monochromatized by graphite single crystal and FTIR (JEOL, JIR-6500). X-ray diffraction analysis was conducted at applied voltage of 40 kV and current of 100 mA.

3. Results and discussion

3.1 Thermal decomposition of BaTiO₃(C₂O₄)₂·4H₂O in air

The TG/DTA curves of BaTiO₃(C₂O₄)₂·4H₂O in air atmosphere are shown in Fig. 3. There exist two endothermic peaks at 117.5 and 706.2°C, a strong exothermic peak at 352.7°C, and a weak exothermic peak at 451.2°C in DTA curve. Obvious weight loss in the temperature range of 40–225°C, 225–440°C and 620–710°C, and low weight loss in the range 440–620°C are observed from TG curve. It can also be found that the four peaks of differential thermal gravimetry (DTG) curve which is the differential of TG curve correspond to these of DTA. This means that decomposition process of BaTiO₃(C₂O₄)₂·4H₂O can be divided into four steps.

The XRD patterns of the samples heated at various temperatures for 2 h are shown in Fig. 4. The patterns of the samples heated from 100 to 440°C are similar to curve (a), shown in Fig. 4, which is the pattern of an amorphous phase. In the pattern of the sample heated at 440°C (Fig. 4 (b)), the peak at d=0.372 nm which is assigned to the 111 peak of BaCO₃ can be observed. With the further increase of temperature, as indicated in Fig. 4 (c), the XRD pattern of an intermediate phase (Ba₂Ti₂O₅CO₃) which accords with that reported by Kumar et al.3) This pattern, however, contains one peak which accords with BaCO₃. The peaks of BaTiO₂ begin to appear from 610°C. On further heating, the intermediate phase disappears. Eventually, BaTiO₃ is completely formed above 650°C, as shown in Fig. 4 (e).

In the previous studies,1)-4) the coexistence of the intermediate phase and BaCO₃ was not reported as thermal decomposition products of the oxalate in air. As the appearance of both intermediate phase and BaCO₃ in the decomposition process was confirmed in this study, the decomposition process of BaTiO₃(C₂O₄)₂·4H₂O should be considered again. Let us suppose that the composition of intermediate phase is Ba₂Ti₂O₅CO₃ proposed by Murthy et al.2) According to the results mentioned above, the decomposition of BaTiO₃(C₂O₄)₂·4H₂O at a heating rate of 10°C/min is divided into the four steps as follows.

(1) \[ \text{BaTiO}_3(\text{C}_2\text{O}_4)_2·4\text{H}_2\text{O} \rightarrow \text{BaTiO}_3(\text{C}_2\text{O}_4)_2+4\text{H}_2\text{O} \] (amorphous)

(2) \[ \text{BaTiO}_3(\text{C}_2\text{O}_4)_2 \rightarrow \frac{2}{2} \text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3+2\text{CO}+3/2\text{CO}_2 \] (amorphous)

(3) \[ \text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3 \rightarrow \text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3 \] (crystallization and desorption of CO₂)

(4) \[ \text{BaCO}_3+\text{TiO}_2 \rightarrow \text{BaTiO}_3+\text{CO}_2 \]

The temperature range at each decomposition step depends on the experimental conditions, especially, the raising rate of temperature. The first step is a dehydration process of tetrahydrate. This is an endothermic reaction, corresponding with the peak of DTA at 117.5°C, shown in Fig. 3. The weight loss obtained from TG curve is 16.4% in the step, and well agrees with the theoretical calculating value of 16.0%. The evolution of water vapor in this step is also observed in Mass spectra shown in Fig. 5. The second step is the major event in thermal decomposition. Mass spectra shown in Fig. 5 suggest that the reaction in this step involves simultaneous evolution of carbon monoxide and carbon dioxide. The step includes three reactions, decomposition of BaTiO₃(C₂O₄)₂ to an amorphous intermediate phase (Ba₂Ti₂O₅CO₃) releasing CO and CO₂,
combustion reaction of carbon monoxide with O₂ in air, and reaction of Ba₂Ti₂₅CO₃ with generated CO₂ to form BaCO₃. The adsorption of the free carbon dioxide on the surface of the amorphous intermediate phase can be inferred from FTIR curve (a) shown in Fig. 6, considering that the strong band at 2350 cm⁻¹ is due to the asymmetric stretching vibration of free carbon dioxide. The obvious exothermic peak of DTA in the step is considered to be combustion reaction of carbon monoxide with O₂. This exothermic peak is also considered to be due to the reaction of anhydrous BaTiO(C₂O₄)₂ with O₂, but considering that a big weight loss takes place at slightly lower temperature than the exothermic peak of DTA as shown in Fig. 3, this possibility is denied. The formation of BaCO₃ is attributed to the reaction of the amorphous intermediate phase with CO₂.

The third step is a crystallization process of the amorphous intermediate phase, accompanied by desorption of CO₂ on the surface of the amorphous intermediate phase. Crystallization process is exothermic, corresponding to exothermic peak of DTA at 451.2°C shown in Fig. 3. The FTIR spectrum of the sample with the intermediate phase is shown in Fig. 6 (b). The peaks at 1432, 860 and 700 cm⁻¹ are attributed to CO₃⁻² group of carbonate. The fourth step is the formation of BaTiO₃ due to the reaction of BaCO₃ with Ti₂ and the decomposition of intermediate phase (Ba₂Ti₂O₅CO₃). Both two reactions in this step are endothermic, corresponding to the peak of DTA at 706.2°C shown in Fig. 3, accompanied by evolution of CO₂.

3.2 Decomposition process in N₂ atmosphere

The TG/DTA curves of BaTiO(C₂O₄)₂·4H₂O in N₂ atmosphere are shown in Fig. 7. The peaks at 102.2, 507.1 and 730.8°C in DTA curve correspond to 117.5, 451.2 and 706.2°C of DTA curve in air in Fig. 3, respectively. The peak at 339.8°C in N₂ atmosphere is, however, endothermic, and different from exothermic peak at 352.7°C in air. This fact also suggests that the exothermic peak at 352.7°C in air atmosphere is due to the combustion reaction of CO with O₂. The XRD patterns of the specimens heated at 600°C for 2h in N₂ atmosphere and at 590°C for 2h in air atmosphere are shown in Figs. 8(a) and 8(b), respectively, so as to compare their difference. An obvious difference between patterns (a) and (b) is that the specimen in N₂ atmosphere does not include the peak at d=0.372 nm, according with the maximum diffraction peak of BaCO₃. That is to say, the XRD pattern reported by Kumar et al.³ contains the peak of BaCO₃. The FTIR spectrum of intermediate phase obtained in N₂ atmosphere shown in Fig. 6(c), is the same with that in air. This further suggests that the intermediate is carbonate.

As a combustion reaction did not occur and BaCO₃ did not appear in decomposition process of oxalate in N₂ atmosphere, the decomposition process in N₂ atmosphere is considered as follows.

\[
\begin{align*}
(1) \quad \text{BaTiO(C}_2\text{O}_4)_{\frac{2}{3}}\cdot4\text{H}_2\text{O} & \xrightarrow{40-225^\circ C} \text{BaTiO(C}_2\text{O}_4)_{\frac{2}{3}}+4\text{H}_2 \\
(2) \quad \text{BaTiO(C}_2\text{O}_4)_{\frac{2}{3}} & \xrightarrow{225-480^\circ C} \frac{1}{2}\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3+2\text{CO}+3/2\text{CO}_2
\end{align*}
\]

(3) \quad \frac{1}{2}\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3 \xrightarrow{480-700^\circ C} \frac{1}{2}\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3

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Decomposition temperature of the intermediate phase in BaTiO₃ in air is 706°C and, simultaneously, BaTiO₃ is also produced due to the reaction of BaCO₃ with TiO₂. On the other hand, decomposition temperature of intermediate phase into BaTiO₃ in N₂ is 730.8°C. Comparing DTA peaks and DTG peaks in the two atmospheres, these peaks in air are broad, while those in N₂ are sharp. Whether the difference of decomposition temperature between the two atmospheres is meaningful or not, is considered below.

At a heating rate of 10°C/min, supposing that crystallite size of intermediate phase in air is the same as that in N₂, the difference between decomposition temperatures in air and N₂ is meaningful. In the fourth step of reaction in air, though it could be not confirmed, BaTiO₃, first, is formed due to the reaction of BaCO₃ with TiO₂. It is considered that decomposition of intermediate phase is induced by nuclei of BaTiO₃ formed by the reaction of BaCO₃ with TiO₂. This can interpret the phenomenon that the peaks of DTA and DTG in air are broader than those in N₂. Next, let us consider the effect of crystallite size of intermediate phase. The crystallization temperature of intermediate phase in N₂ and in air is 507.1°C and 451.2°C, respectively. As the crystallite size becomes larger at the higher crystallization temperature, in general, the decomposition temperature in N₂ is drifted into higher temperature side than that in air. Therefore, the effect of crystallite size of the intermediate phase on the decomposition temperature could not be supported strongly.

3.3 The stability of the intermediate phase

The XRD pattern of the specimen heated at 590°C for 2 h in air is shown in Fig. 9(a). This pattern indicates the formation of the intermediate phase, identified as Ba₂Ti₂O₅CO₃ by Kumar et al. The XRD patterns of the intermediate phase exposed at room temperature in air for 20 d and 30 d are shown in Figs. 9(b) and 9(c), respectively. The peak of BaCO₃ after exposition for 20 d obviously increases, while the peak of intermediate phase decreases. There only exist the peaks of BaCO₃ in the XRD pattern in air for 30 d. That is to say, the intermediate phase exposed in air for 30 d is almost completely converted into BaCO₃ and TiO₂. No peaks of TiO₂ in these XRD patterns are observed. This may be because the particles of TiO₂ are too fine or amorphous. Whether the intermediate phase is decomposed into BaCO₃ and TiO₂ or not depends on the partial pressure of carbon dioxide (P_CO₂) in accordance with the following Reaction (1).

\[
\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3\rightarrow\text{Ba}_2\text{Ti}_2\text{O}_5 + \frac{1}{2}\text{CO}_2
\]

(4) 1/2Ba₂Ti₂O₅CO₃ → BaTiO₃ + 1/2CO₂

Decomposition process of oxalate in air and N₂ at 500°C for 2 h was determined by weight analysis from BaTiO₃(C₂O₄)₂·4H₂O heated at 400°C over 7 d and BaCO₃ is included. Therefore, the composition of intermediate phase is not necessarily Ba₂Ti₂O₅CO₃. The obtainment of a stable phase, accurate decide of composition and crystal structure about intermediate phase are the further problems.

4. Conclusions

Decomposition process of oxalate in air and N₂ atmospheres was investigated in the study. The main results are summarized as follows.

(1) Not only the intermediate phase but also BaCO₃ and TiO₂ are produced in decomposition process of oxalate in air. The BaTiO₃ formation in air atmosphere is due to the reaction of BaCO₃ with TiO₂ and the decomposition of intermediate phase.

(2) The BaTiO₃ formation in N₂ atmosphere is only assigned to the decomposition of intermediate phase.

(3) The intermediate phase does not contain the peak which is in accord with BaCO₃.

The composition of intermediate phase obtained in air was determined by weight analysis from BaTiO₃(C₂O₄)₂·4H₂O heated at 400°C over 7 d and BaCO₃ is included. Therefore, the composition of intermediate phase is not necessarily Ba₂Ti₂O₅CO₃. The obtainment of a stable phase, accurate decide of composition and crystal structure about intermediate phase are the further problems.

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