

## Morphology of Barium Titanyl Oxalate Particles Produced by Homogeneous Precipitation

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Spherical, submicrometer particles of barium-titanyl oxalate were homogeneously precipitated by thermal decomposition of diethyl oxalate in acidic aqueous solutions. The rates of oxalate ion generations, determined by various combinations of temperature and initial concentration of diethyl oxalate had a very important effect on the particle size distribution. Monosized, bimodal, or broad unimodal powders were obtained under certain combinations of experimental variables.

### Introduction

Barium titanate (BT) is an attractive material as its ceramics are widely used as main constituents of electroceramic components such as multilayer capacitors and nonlinear resistors.<sup>1,2</sup> When such polycrystalline materials are used for applications such as these, a uniform final microstructure is needed as the advantage of processing for monosized powders.<sup>3</sup> For the reasons, BT powders as the starting material need to have a uniform particle size and shape in order to produce high-quality ceramics. Similarly, the powders of barium titanyl oxalate (BTO), known as the precursor material of BT, need to have a uniform particle size and shape. Consequently, the ability to control precipitation variables is necessary to yield BTO powders with spherical and specific particle size.

Since Clabaugh *et al.*<sup>4</sup> reported that the precipitates of BTO can be converted to a high purity barium titanate of nearly perfect stoichiometry, BTO has variously been prepared as follows. Wet preparation techniques are usually adopted for the preparation of micrometer-sized spherical particles.<sup>5-7</sup> Recently, present authors also reported a number of methods for preparation of uniform BTO particles,<sup>8-10</sup> one of which was prepared by homogeneous precipitation. This procedure involved dissolution of barium chloride and titanium tetrachloride in aqueous solution and precipitation of BTO by thermal decomposition of diethyl oxalate (DEO).<sup>10</sup> However, no consideration was given to the effects of reaction conditions on the particle morphology of BTO.

The main objective of this work was to investigate the influence of experimental variables such as supporting anions, concentrations of precipitating agents, precipitating temperature and aging time on the particle morphology of precipitates.

### Experimental Procedure

**Precipitation.** Stock solution of barium chloride (99% pure, Katayama Chem. Co.) was prepared by dissolving the salt in deionized water so as to produce a barium ion concentration of about 0.2 M. Stock solution of titanium tetrachloride (reagent grade, Yakuri Chem. Co.) was prepared by adding a 160 mL volume slowly to a cold distilled water stirred rapidly and diluting to 1 L. Exact titanium content

was determined gravimetrically by the hydroxide precipitation method.<sup>11</sup> The final solution was stored in a refrigerator.

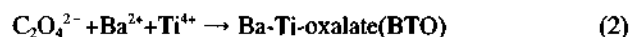
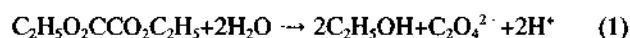
Supporting anions used for chloride and nitrate solutions were adjusted to 0.1 M. Cation stock solution and solution of the supporting anion were added to a beaker in predetermined quantities along with a sufficient amount of distilled water to bring the total volume slightly less than 200 mL. The beaker was covered and placed in an isothermal bath that was set at the desired temperature. The predetermined amount of DEO (reagent grade, Katayama Chem. Co.) was added. Solution volume was brought to exactly 200 mL. The time to onset of precipitation, manifested as the appearance of bluish tint, was recorded for each experiment. Small aliquots were collected and quenched to 0 °C at regular intervals to observe development of particle morphology on various aging times and growth kinetics.

Initial barium and titanium concentrations,  $[Ba^{2+}]_0$  and  $[Ti^{4+}]_0$ , were kept constant at 0.02 M in all experiments, while initial DEO concentration was varied to give  $[DEO]_0 / ([Ba^{2+}]_0 + [Ti^{4+}]_0)$  ratios of 2, 4 and 8. The pH of the supporting anion for nitrate and chloride was remained constant at 1.2 possibly due to buffering action of oxalate ions with other ions in the solutions.

**Characterization.** The particles were separated from the supernatant liquids by centrifugations and washed twice with deionized water and twice with ethanol. During the ethanol wash, particles were dispersed with a sonic disruptor. A drop of suspension in ethanol was placed on aluminum foil and dried for observations of morphology by scanning electron microscope (JEOL JSM-5800 LV).

### Results and Discussion

As DEO slowly decomposed, white oxalate precipitates were formed. The decompositions of DEO and the formation of BTO occurred by the following reactions.



The rate determining step in the above two reactions is the decomposition of DEO. A rate expression of the rate determining step of DEO decomposition at constant pH is fol-

lowed as,

$$-d[\text{DEO}]/dt = k[\text{DEO}] \quad (3)$$

$$k = (\ln[\text{DEO}]_0 - \ln[\text{DEO}])/t \quad (4)$$

where  $k$  is the rate constant of DEO decomposition,  $[\text{DEO}]_0$

**Table 1.** Variation of generation rate for oxalate ion with various experimental conditions

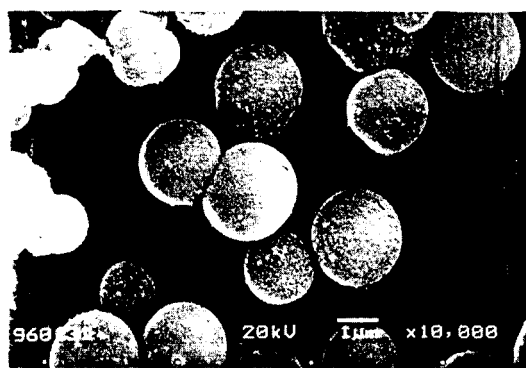
Supporting anion	Temperature (°C)	$\frac{[\text{DEO}]_0}{([\text{Ba}^{2+}]_0 + [\text{Ti}^{4+}]_0)}$	rate to nucleation ( $\text{min}^{-1}$ )
$\text{NO}_3^-$	50	2	0.19
		4	0.28
		8	0.35
	60	2	0.52
		4	0.71
		8	0.86
	70	2	0.92
		4	1.00
		8	1.00
$\text{Cl}^-$	50	2	0.22
		4	0.29
		8	0.35
	60	2	0.50
		4	0.57
		8	0.86
	70	2	0.92
		4	1.00
		8	1.20

the initial concentration of DEO,  $[\text{DEO}]$  is the concentration of DEO at any time  $t$ . Generally, rate constant, especially decomposition rate of DEO in this study, depends on temperature like as Arrhenius equation ( $k \propto e^{-1/T}$ ).

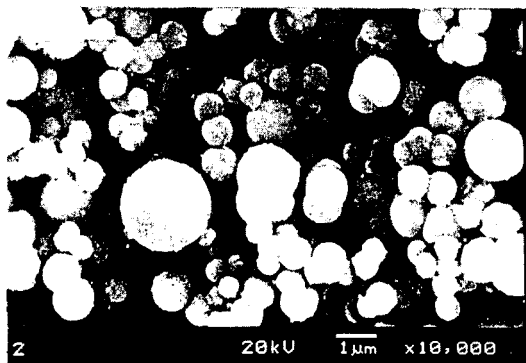
The oxalate precipitation was started with critical supersaturation for particular combination of experimental variables such as the initial concentration of DEO, temperature, concentration of barium and titanium, and pH. As the concentrations of barium and titanium were kept constant at 0.02 M and pH of the reaction systems was also kept constant at 1.2, the critical supersaturation for supporting anion systems of chloride and nitrate depends on the initial concentration of DEO and temperature.

The reciprocal time to reach critical supersaturation is related to generation rate of oxalate ion, which was defined it as the "rate-to-nucleation" (RN).<sup>12,13</sup> Rate-to-nucleation measured in various experimental conditions are listed in Table 1. The higher temperature and the higher initial concentration of DEO are, the faster rate-to-nucleation for BTO is. The results are similar with the behavior of the rate-to-nucleation for ZnS powders by homogeneous precipitation.<sup>12</sup> The significant difference of the rate-to-nucleation has not been found between nitrate and chloride supporting anion systems.

Figure 1 shows SEM micrographs of oxalates taken after 60 min of aging time ( $T=50^\circ\text{C}$ , supporting anion of  $\text{Cl}^-$ , and (a)  $[\text{DEO}]_0/([\text{Ba}^{2+}]_0 + [\text{Ti}^{4+}]_0) = 4$ , (b)  $[\text{DEO}]_0/([\text{Ba}^{2+}]_0 + [\text{Ti}^{4+}]_0) = 8$ ). Either monosized, bimodal or continuous distribution of particle sizes were obtained in chloride system, depending on the value of ratio  $[\text{DEO}]_0/([\text{Ba}^{2+}]_0 + [\text{Ti}^{4+}]_0)$ . At

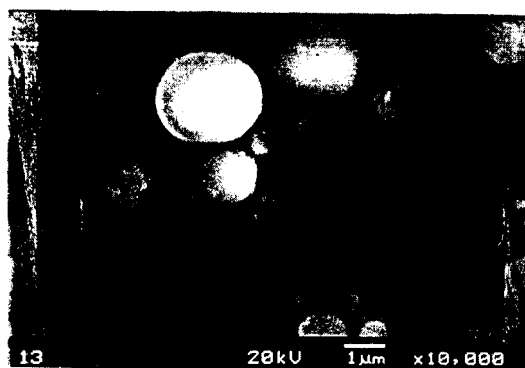


(a)

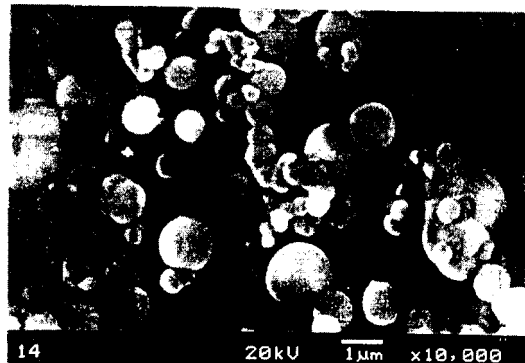


(b)

**Figure 1.** Micrographs of precipitates obtained in supporting anion of chloride with aging time of 60 min at temperature of 50 °C and  $[\text{DEO}]_0/([\text{Ba}^{2+}]_0 + [\text{Ti}^{4+}]_0)$  of (a) 4 and (b) 8.



(a)

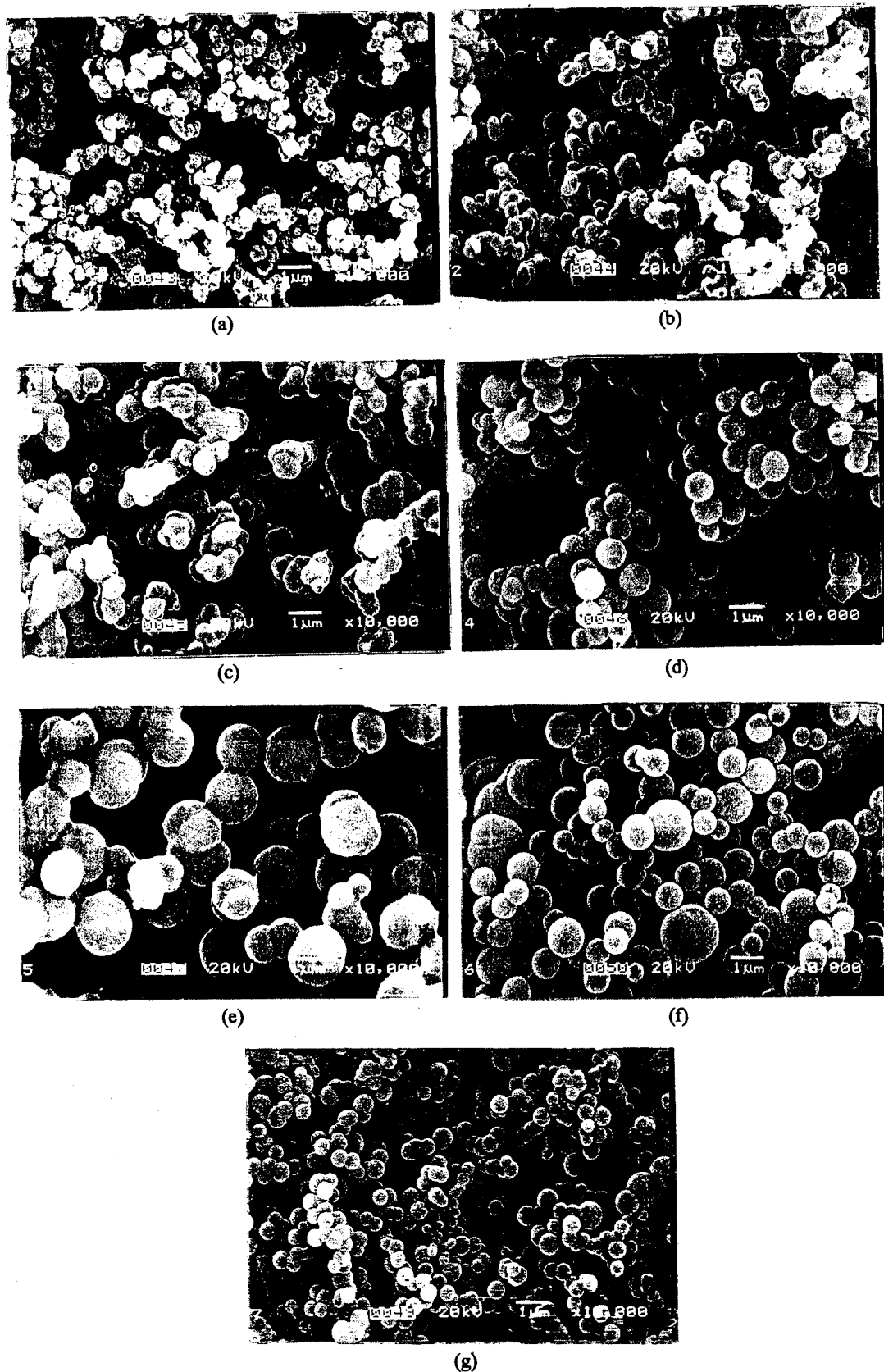


(b)

**Figure 2.** Micrographs of precipitates obtained at temperature of 70 °C and  $[\text{DEO}]_0/([\text{Ba}^{2+}]_0 + [\text{Ti}^{4+}]_0)$  of 4 in supporting anion of nitrate with aging time of (a) 30 min and (b) 60 min.

the ratio of 4, monosized particles were observed (Figure 1(a)), probably because growth process of particles is predo-

minant. At higher ratio of 8, bimodal particles were obtained (Figure 1(b)). The occurrence of bimodal particle mor-



**Figure 3.** Micrographs of precipitates obtained at temperature of 50 °C and  $[DEO]_0/([Ba^{2+}]_0+[Ti^{4+}]_0)$  of 4 in supporting anion of nitrate with aging time of (a) 30 min, (b) 45 min, (c) 60 min, (d) 75 min, (e) 90 min, (f) 105 min and (g) 120 min.

**Table 2.** Mean particle size distribution at T=50 °C

concentration ratio [DEO] <sub>0</sub> /([Ba <sup>2+</sup> ] <sub>0</sub> + [Ti <sup>4+</sup> ] <sub>0</sub> )	2		4		8	
	Supporting anion aging time	Cl	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
30	monosized	monosized	monosized	monosized	broad unimodal	monosized
	0.5 μm	0.5 μm	0.5 μm	0.7 μm	0.7 μm	0.7 μm
60	monosized	monosized	monosized	broad unimodal	bimodal	bimodal
	1.0 μm	2.5 μm	2.0 μm	1.0 μm, 2.0 μm	0.8 μm, 2.0 μm	0.7 μm, 1.5 μm
90	bimodal	bimodal	bimodal	bimodal	broad continuous distribution	
	0.5 μm, 1.8 μm	0.5 μm, 2.0 μm	0.5 μm, 2.0 μm	0.5 μm, 2.0 μm		

phology suggests that a second generation of particles forms as a direct consequence of growth rate not keeping up with oxalate ion generation.

Another perhaps more sensitive parameter on the particle size distribution is the temperature for nucleation. At higher temperature above 60 °C, generation of oxalate ion was so rapid that particle size decreased and the degree of agglomeration increased. The powders were agglomerates of 0.3-1.3 μm particles, and significant necking between particles was evident (not shown).

An aging time after nucleation of oxalate has very important influence on the particle size distribution of powders. Figure 2 shows micrographs of oxalates obtained with aging time of 30 and 60 min at 70 °C for supporting anion of nitrate and [DEO]<sub>0</sub>/([Ba<sup>2+</sup>]<sub>0</sub>+ [Ti<sup>4+</sup>]<sub>0</sub>) of 2. The change of morphology occurred at shorter aging time than that at 50 °C even under condition of lower DEO concentrations. At lower temperature of 50 °C, spherical particles were observed. As temperature increased, both degree of agglomeration and rate of oxalate ion generation were so high that optimization of growth rate was too difficult to find.

Table 2 gives the result of particle size distribution measured at various aging times and the initial concentrations of DEO in nitrate and chloride supporting anion systems at 50 °C. The results showed that unimodal particle size distribution is obtained at aging time of 30 min. At longer aging time of 60 min and lower DEO concentration ratio of 2 and 4, unimodal distribution was still obtained with larger particles (first generation) having a mean size of about 1.0-2.5 μm. At further longer aging time of 120 min and high DEO concentration ratio of 8, bimodal size distribution was obtained. As shown in Tables 1 and 2, the significant difference of the rate to nucleation and particle morphology has not been found between chloride and nitrate supporting anion systems.

Further detail studies for aging time were carried out under the condition of temperature of 50 °C and [DEO]<sub>0</sub>/([Ba<sup>2+</sup>]<sub>0</sub>+ [Ti<sup>4+</sup>]<sub>0</sub>) of 4 in supporting anion of nitrate. A 15 min interval was taken for the aging time in the experiment. The micrographs of oxalate obtained with various aging times are shown in Figure 3. When the aging time was shorter than 60 min, the powders were agglomerates of particle and necking between particles is evident as shown in Figure 3(a)-(c). At aging time of 75 min, monosized and spherical particles were observed (Figure 3(d)) and the same morphology was still observed until the aging time of 90 min, having larger particles with some necking (Figure

3(e)). At longer aging time of 120 min, broad unimodal particles were observed (Figure 3(g)).

### Conclusion

Formation of uniform spherical particles of barium-titanyl oxalate was investigated with first consideration of the influence of experimental variables on the morphology. Rate-to-nucleation was faster with higher temperature and with higher values of [DEO]<sub>0</sub>/([Ba<sup>2+</sup>]<sub>0</sub>+ [Ti<sup>4+</sup>]<sub>0</sub>). The particle size distribution was found to be controlled by the generation rate of oxalate ions, irrespective of the value of the temperature and of [DEO]<sub>0</sub>/([Ba<sup>2+</sup>]<sub>0</sub>+ [Ti<sup>4+</sup>]<sub>0</sub>). Spherical barium-titanyl oxalate powders with desired size distribution were found to be produced at 50 °C and [DEO]<sub>0</sub>/([Ba<sup>2+</sup>]<sub>0</sub>+ [Ti<sup>4+</sup>]<sub>0</sub>)=4.

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