



## Synthesis Mechanism of Nano BaTiO<sub>3</sub> Particles at Low Temperature by Molten Salt Method†

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Using the molten salt method, nano BaTiO<sub>3</sub> can be synthesized at 150 °C and atmospheric pressure for thick film application. It was reported that this is a result of the moisture in the air being absorbed in the salt. However, the precise mechanism of the nano BaTiO<sub>3</sub> particle synthesis at such low temperature, air and atmospheric pressure has not been presented yet. Therefore, by observing the intermediate stage of the synthesis through varying the synthesis time at the low temperature of 150 °C, experimental results regarding the synthesis process were obtained. Experimental results showed that BaTiO<sub>3</sub> powder below 20 nm was synthesized when synthesis was conducted over 10 h using the molten salt method employing KOH-KCl mixed salt at 150 °C. By varying the synthesis time from 1 to 10 h, the microstructure and XRD phase analysis results revealed that the mixed salt does not melt overall and the moisture in the air is absorbed in the salt to form an oxalate coating layer. The mechanism where nano BaTiO<sub>3</sub> is synthesized through the dissolution and reaction of the base materials BaCO<sub>3</sub> and TiO<sub>2</sub> in the coating layer is discussed here.

**Keywords:** Ceramics, Dielectrics, Melting, Salt.

### INTRODUCTION

BaTiO<sub>3</sub>, a representative ferroelectric material, is used in various electronics industries. Recently, in order to create a thinner dielectric layer based on the trend of making electronic components like MLCC more light weight and smaller in size, many studies to apply nano BaTiO<sub>3</sub> particles are being conducted<sup>1</sup>. Although broad studies on sintering and dielectric properties are in demand with the expansion of nano dielectric particle application, the synthesis and control of the nano particles is not yet convenient, so there are no sufficient reports available. Manufacturing methods of BaTiO<sub>3</sub> powder, including hydrothermal synthesis<sup>2</sup>, oxalate method<sup>3</sup> and solid phase method<sup>4,5</sup> are mainly used in the industry. Various methods to mass synthesize BaTiO<sub>3</sub> particles of 150 nm have been commercialized. However, there is no clear synthesis method for dispersed BaTiO<sub>3</sub> particles below approximately 20 nm, as well as no sufficient research results reported. In particular, research on nano particle synthesis using the molten salt method<sup>6</sup> that synthesizes nano BaTiO<sub>3</sub> particles through the moisture absorption of water under the low temperature of around 150 °C and atmospheric pressure is lacking.

Therefore, in this study, the trends based on the synthesis time at low temperature using the molten salt method were evaluated and the nano BaTiO<sub>3</sub> of a primary particle size below 20 nm and reproducibility was synthesized. Also, a mechanism that allows the synthesis of nano BaTiO<sub>3</sub> particles at low temperature where salt does not melt and produces nano particles is to be presented. The variation in nano BaTiO<sub>3</sub> shape according to the synthesis time was observed through both the electron microscopy and analysis of the electron microscopy after cutting a cross section using FIB. This makes the shape and composition of the salt and nano BaTiO<sub>3</sub> directly observable. Based on these results, the synthesis process of nano BaTiO<sub>3</sub> will be explained.

### EXPERIMENTAL

The base materials used were BaCO<sub>3</sub> (99 %, Daejung C & M Co. Ltd., Korea), TiO<sub>2</sub> (99 %, N & A Materials Co. Inc., USA), KOH (85-100 %, Daejung C & M Co. Ltd., Korea) and KCl (99 %, Daejung C & M Co. Ltd., Korea). The synthesis method of nano BaTiO<sub>3</sub> was the molten salt method reported by Park *et al.*<sup>7</sup>. The initial materials used were the aforementioned

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base material powder to mix  $\text{BaCO}_3$  and  $\text{TiO}_2$  at the mole fraction of 1:1 and for the molten salt,  $\text{KOH-KCl}$  was mixed at the mole fraction of 1:1. Then, the mixed starting materials and molten salt was mixed at the mole fraction of 1:25 and placed in a crucible where the temperature was raised to  $150^\circ\text{C}$  at the rate of  $10^\circ\text{C}/\text{min}$ . The crucible temperature was maintained at  $150^\circ\text{C}$  for 1, 5 and 10 h and then cooled to synthesize nano  $\text{BaTiO}_3$ . The synthesized  $\text{BaTiO}_3$  powder was cleaned with distilled water more than 3 times. Phase analysis was conducted using XRD and the particle shape was observed using FE-SEM (JSM 6700F, Jeol, Japan). In order to observe the nano  $\text{BaTiO}_3$  synthesis mechanism, the salt powder was cut using FIB when the salt was not cleaned and the cross section was observed using an electron microscope.

## RESULTS AND DISCUSSION

Fig. 1 shows the FE-SEM images of the base powder materials  $\text{BaCO}_3$  and  $\text{TiO}_2$ , as well as the synthesized nano  $\text{BaTiO}_3$ . The particle size of  $\text{BaCO}_3$ , as shown in Fig. 1(a), was 500 nm and the particle size of  $\text{TiO}_2$  was approximately 10 nm, as shown in Fig. 1(b). When using  $\text{TiO}_2$  in the order of a few hundred nm, the dissolution rate of the salt is low and previous experiments found that sufficient synthesis did not occur. As a result, in order to use base materials of a maximum specific surface area, commercial  $\text{TiO}_2$  nano particles were used, as shown in the figure<sup>8</sup>. However, it was found that the particles were severely agglomerated. Fig. 1(c) shows the nano  $\text{BaTiO}_3$  synthesized using the  $\text{TiO}_2$  nano particles as the base material. The particle size was observed to be approximately below 20 nm and were observed to be agglomerated as well. However, the primary particles could be relatively easily identified through observation, which are thought to be the result of soft agglomeration caused by the salt cleaning process.

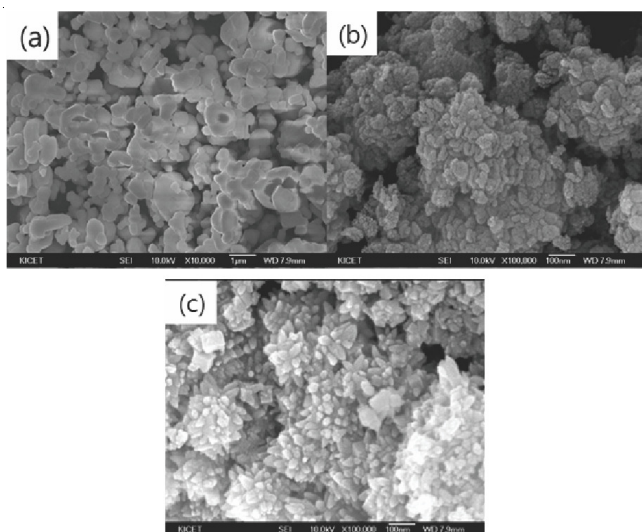


Fig. 1. SEM images of source materials and synthesized nano particle: (a)  $\text{BaCO}_3$ , (b)  $\text{TiO}_2$ , (c) synthesized nano  $\text{BaTiO}_3$

Fig. 2 is the XRD phase analysis results according to the synthesis time. In Fig. 2(a), the peaks of the unreacted materials  $\text{BaCO}_3$  and  $\text{TiO}_2$  were observed for the case of 1 h synthesis at  $150^\circ\text{C}$  and it could be seen that the  $\text{BaTiO}_3$  peak is not developed. This is thought to be a result of the heating duration

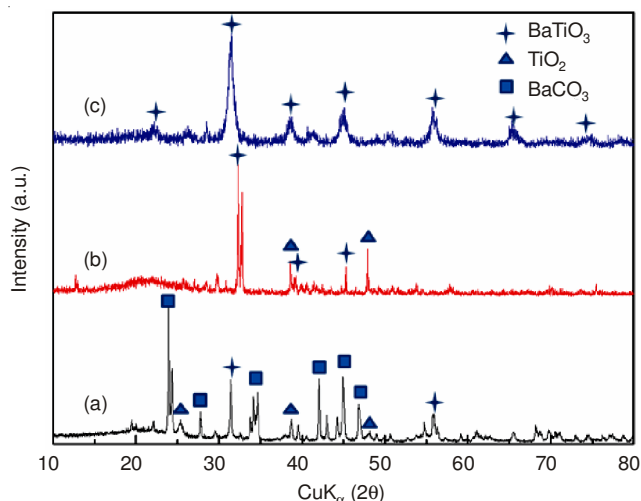


Fig. 2. X-Ray diffraction patterns of powders synthesized by molten salt method at  $150^\circ\text{C}$  with reaction time: (a) 1 h, (b) 5 h and (c) 10 h

being too short for sufficient dissolution of the base material powder in the salt as the synthesis time was short. In Fig. 2(b), when the synthesis maintenance time was increased to 5 hours, the peak of the unreacted  $\text{BaCO}_3$  was almost nonexistent and the  $\text{TiO}_2$  peak was reduced. The development of the synthesized  $\text{BaTiO}_3$  peak was observed. However, the  $\text{BaTiO}_3$  peak was also not measured in a distinct form of intensity, but rather appeared as an unstable pattern. This signifies poor crystallinity of the synthesized nano  $\text{BaTiO}_3$ <sup>9-12</sup>. Finally, it is observed in Fig. 2(c) with a synthesis time of 10 h that a stable  $\text{BaTiO}_3$  phase was formed, but in the  $20$  to  $30^\circ$  region, weak peaks for the unreacted  $\text{BaCO}_3$  and  $\text{TiO}_2$  were observed. This observation is thought to be the unreacted remainder of the base material powder due to the local non-uniformity in the moisture absorption amount, even though the absorption of moisture in the air by the salt causes synthesis at low temperatures.

Fig. 3 shows the salt powder surface observed using FE-SEM according to the synthesis time with the salt not cleaned. In Fig. 3(a), which shows the 1 h synthesis time at  $150^\circ\text{C}$ , a large lump of salt with a smooth surface and an agglomeration of 10 nm order particles can be observed together. From the XRD phase analysis results of Fig. 2, it can be determined that the small nano particles are unreacted  $\text{TiO}_2$  and as no 500 nm order  $\text{BaCO}_3$  particles were observed, it was thought that the  $\text{BaCO}_3$  is rapidly being dissolved into the salt. For the case of the 5 h synthesis time shown in Fig. 3(b), there was a uniform formation of small particles that seem to be  $\text{BaTiO}_3$  nuclei on the salt surface. This phenomenon is predicted to be the formation of nuclei in the extraction process of a new phase with the supersaturation of the base material within the liquid salt. The salt powder after 10 h of synthesis is shown in Fig. 3(c). It was found that the nuclei formed on the salt surface grew to larger sized particles. However, these particles formed on the salt surface is not of separated and independent particles, but nuclei attached to a large salt particle. It was predicted that when the salt is cleaned, each particle would separate, as shown in Fig. 1(c). Also, based on the crystal structure change of Fig. 2 and the salt surface shape change of Fig. 3, it was estimated that the synthesis of nano  $\text{BaTiO}_3$  at low temperatures requires a synthesis time of 10 h.

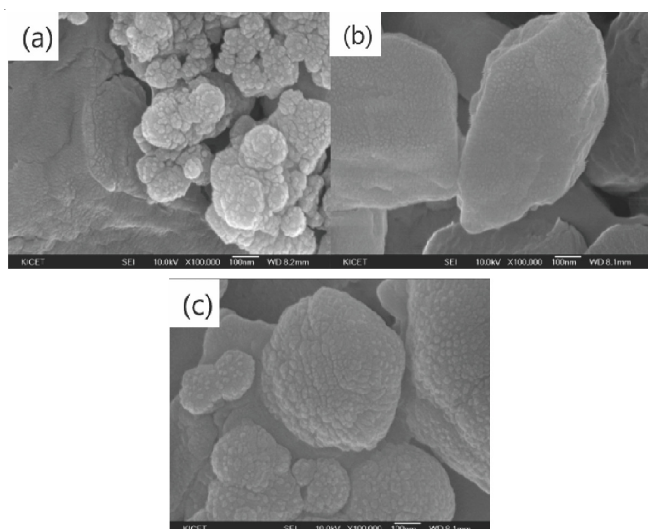


Fig. 3. SEM images of application Molten salt method with reaction time: (a) 1 h, (b) 5 h, (c) 10 h

Fig. 4 is a diagram proposed according to the synthesis time based on the above results. For the established molten salt method, synthesis has to be conducted at temperatures above 400 °C where salt melts<sup>13</sup>. However, in this study, synthesis occurred at 150 °C. This was due to the absorption of moisture in the air by the salt during the mixing process between the salt and base materials. The absorbed moisture by the salt, as shown in Fig. 4(a), also formed a thin oxalate coating layer on the salt surface. The basis for this conclusion was that the salt was not sufficiently dissolved overall based on the particle state being maintained to a certain degree. Also, when the temperature is increased in this state, BaCO<sub>3</sub>, which dissolves better with salt, can be dissolved by the oxalate layer, as shown in Fig. 4(b). TiO<sub>2</sub>, which also has a low solubility, can gradually dissolve to react within the salt, as shown in Fig. 4(c), to result in the synthesis of nano BaTiO<sub>3</sub> at the dissolved oxalate coating layer of the salt surface.

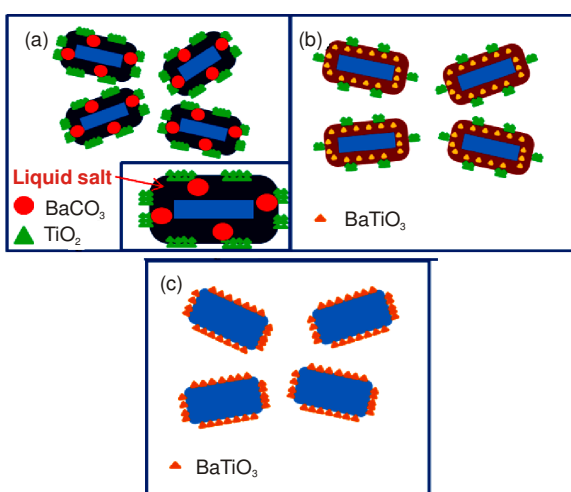


Fig. 4. Schematic diagram of synthesis mechanism by molten salt method with reaction time: (a) 1 h, (b) 5 h, (c) 10 h

To verify the presented diagram, FIB was used to first cut the cross section of the salt and then the salt particle surface using FE-SEM. This is shown in Fig. 5. The inside of the cross

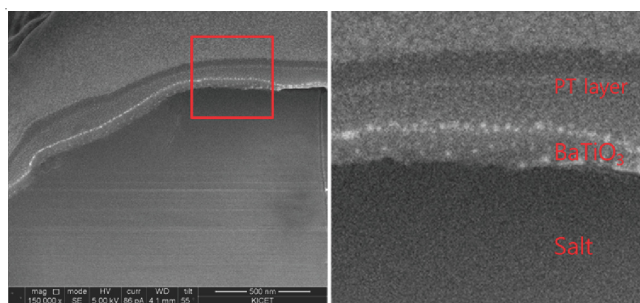


Fig. 5. SEM images of a FIB-prepared cross-section of synthesized salt

section cut salt was uniform and the image was in agreement with the prediction of Fig. 4 that nano particles are not synthesized inside the salt. In addition, like the diagram presented, uniform and separated nano BaTiO<sub>3</sub> particles below 20 nm with nuclei formed are found only on the salt surface and it was observed that layers of the particles were formed. This signifies that synthesis proceeds with salt in a state of no melting overall at 150 °C and the results of Figs. 2 and 3 confirms the overall mechanism of Fig. 4.

### Conclusion

Using the molten salt method, nano BaTiO<sub>3</sub> was synthesized at 150 °C for over 10 h with the synthesized particle size being lower than 20 nm. In order to identify the mechanism of nano BaTiO<sub>3</sub> synthesis at low temperatures, FIB was used to cut the cross section of the synthesized salt. Then, FE-SEM was used to observe the salt surface, revealing a layer of nano BaTiO<sub>3</sub> formed 20 nm below the salt surface. Based on the observations, this study proposed a mechanism of nano BaTiO<sub>3</sub> synthesis at temperatures below the melting point. This is due to the formation of a coating layer of dissolved KOH through the absorption of moisture and the reaction of the base materials BaCO<sub>3</sub> and TiO<sub>2</sub> at the liquid coating layer.

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