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Effect of Water in the Synthesis of Nano $BaTiO_3$ Particle Using Potassium Hydroxide†

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The synthesis conditions of low reaction temperature and normal pressure must be satisfied to improve dispersion and to facilitate the control of nano particle size. Based on this, the low temperature synthesis conditions of nano $BaTiO_3$ particles were investigated using the molten salt method. Nano $BaTiO_3$ particles were synthesized using KOH and KOH-KCl and the results of the different types of salt were compared. The potential synthesis at low temperature was also assessed according to the addition of water. The nucleation of $BaTiO_3$ particles and growth of particles were promoted in the case of KOH-KCl compared to that of KOH. In the case of the KOH-KCl, sufficient phase synthesis was observed at 200 ºC, which is lower than the melting point of salt of 401 ºC. With the addition of water, phase synthesis occurred among the nano $BaTiO_3$ particles at over 120 ºC in a 7.6 M salt solution. This is thought to be caused by the increased solubility of salt due to the salting-in effect.

Key Words: Powders-chemical preparation, Molten salt, Nano particle, $BaTiO_3$, Titanates.

INTRODUCTION

With the recent increase in the need for nano-particles, there are many research studies being conducted on nano $BaTiO_3$ particles with excellent crystallinity and dispersibility[1,2]. In particular, because it is more advantageous to synthesize nano-sized $BaTiO_3$ particles at low temperature to control its dispersibility and synthesis conditions, nano particles are produced using various types of liquid methods. However, liquid reactions pose the common problems of lower crystallinity of the synthesized $BaTiO_3$ and aggregation of particles. Although there have been many studies on minimizing the particle size, there is still insufficient research on synthesizing nano particles with outstanding crystallinity and dispersibility.

In the molten salt method, which is a type of high-temperature liquid reaction technique, the synthesized particles are obtained through uniform re-precipitation of a new phase in a supersaturated condition after the base material is dissolved by the molten liquid. Because homogeneous nucleation can be induced in the molten salt during this process, this technique is able to control the aggregation of particles[3]. However, it also has a drawback in that it requires the salt used in the synthesis process to be cleaned thoroughly but it cannot be removed completely.

During particle synthesis in the molten salt technique, there is an increase in solubility and supersaturation with an increase of KOH, which has a low melting point and promotes crystallinity. The increased supersaturation, in turn, promotes nucleation and crystal growth during reaction and thereby facilitates particle synthesis at low temperature and produces nano particles with outstanding crystallinity[4]. In addition, when KOH is used with another type of mixed salt, there is an increase in solubility during the dissolution due to the salting-in effect and synthesis occurs over the liquid creation temperature. When the two salts are melted in water, synthesis may occur at a lower temperature than the melting points due to the increase in solubility from the salting-in effect[5]. With respect to the molten salt technique using KOH, Ramdas *et al.*[6] have reported their findings on the study of the synthesis of stannates ($Ba_{1-x}Sr_xSnO_3$, x = 0.0-1.0) particles. However, there are still insufficient reports on diverse compositions and not enough investigations have been conducted on low temperatures at which phase synthesis can occur. Also, no research has been conducted on the effects of added water on the $BaTiO_3$ synthesis at low temperature.

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In this study, nano $BaTiO_3$ particles were synthesized at low temperature through the molten salt method using KOH and KOH-KCl. The reaction temperature with KOH-KCl, the synthesis temperature of nano $BaTiO_3$ particles according to the changes in the salt concentration caused by addition of water and the shape and size of the particles were observed and the phase analysis was performed. Based on the findings, the possibility of synthesizing nano $BaTiO_3$ particles at low temperature using the molten or salt solution method was investigated.

EXPERIMENTAL

To synthesize nano $BaTiO_3$ particles using the molten salt method, $BaCO_3$ (98 %, Junsei Chemical Co. Ltd., Japan) and TiO_2 (99 %, N and A Materials Co. Inc., USA) were used as base materials and KOH (85-100 %, Daejung C & M Co. Ltd., Korea) and KCl (99.5 %, Junsei Chemical Co. Ltd., Japan) were used to produce the molten salt. Mixed salt was prepared by mixing KOH and KCl in 1:1 molar ratio. The salt was mixed with the base materials in a volume ratio of 10:1, respectively, to adjust the synthesis temperature to the melting point of the salt and the nano $BaTiO_3$ powder was synthesized. Then, water was added to KOH-KCl to produce salt solutions with concentrations 1 M, 7.6 M and 15.2 M. The volume mixing ratio of the salt and base materials was fixed at 10:1. The base materials, $BaCO_3$ and TiO_2, were mixed together and were stirred for synthesis in a water bath at a temperature between 100-150 ºC for 1 h. After synthesis, the remaining salt was washed with water at least 3 times and dried at 100 ºC to obtain the synthesized $BaTiO_3$ powder. Phase analysis was performed on the $BaTiO_3$ powder using XRD (D/max 2200V/PC, Rigaku Co., Japan) and the shape and size of the particles were observed using FE-SEM (JSM-6700F, JEOL Ltd., Japan) and TEM (JEM2000EX, JEOL Ltd., Japan).

RESULTS AND DISCUSSION

Fig. 1 shows the results of the XRD analysis on $BaTiO_3$ that was synthesized at 450 ºC for 1 h using KOH-KCl and KOH salts. The melting points of KOH and KOH-KCl were around 400 ºC as shown in the phase diagram of Fig. 2. Thus, setting the temperature at 450 ºC, which is significantly higher than the melting points of the salts, meets the conditions for the $BaTiO_3$ synthesis. In the case of the mixed salt of KOH-KCl, there were no notable abnormalities observed. On the other hand, when KOH was used, there were remnants of one of the base materials, $BaCO_3$, at the end of the reaction. The reaction rate is higher in synthesis reactions when mixed salts are used compared to when single salt is used because of the salting-in effect which causes an increase in solubility due to the presence of another salt[5]. Accordingly, a relatively better outcome resulted in the synthesis reaction using KOH-KCl than the reaction using KOH in the same synthesis time. However, because $BaTiO_3$ was also sufficiently synthesized when KOH was used, it is thought that that it is possible to obtain single-phase $BaTiO_3$ powder by controlling the mixing ratio of the base materials.

Fig. 3 is the SEM and TEM photos of $BaTiO_3$ powder that was synthesized at 450 ºC for 1 h using the KOH-KCl and

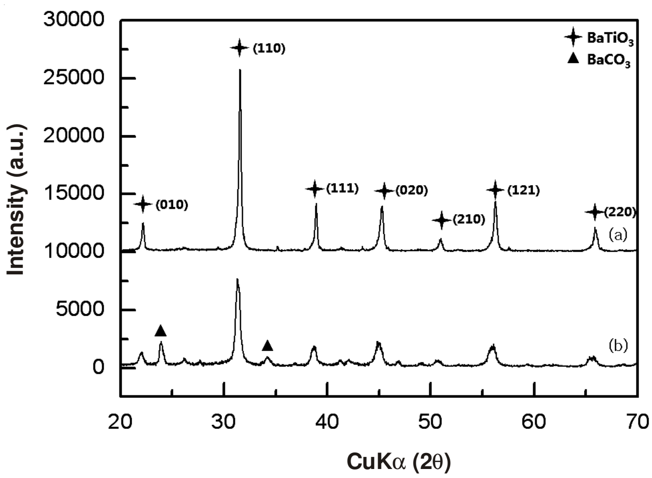

Fig. 1. XRD patterns of $BaTiO_3$ powders synthesized at 450 ºC for 1 h with the variation of salt (a) KOH-KCl and (b) KOH

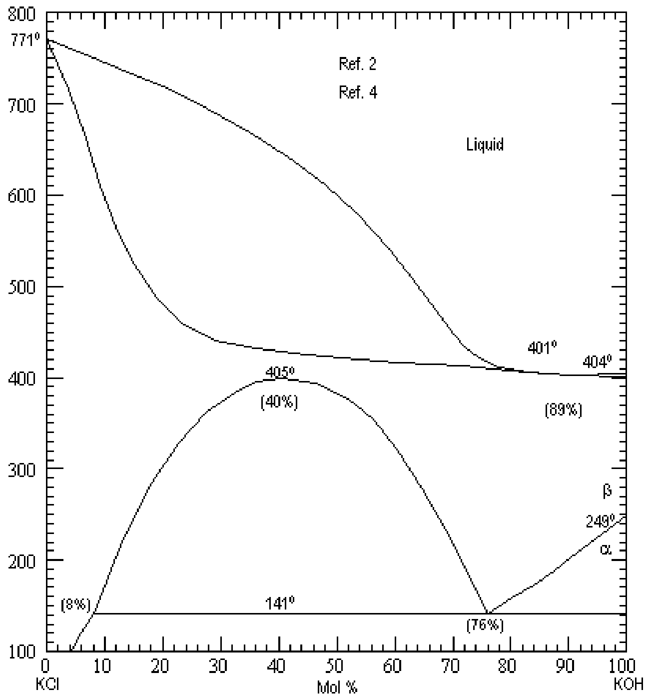

Fig. 2. Phase diagram of KOH-KCl[9]

KOH salts shown in Fig. 1. Bigger particles were synthesized in the reaction using the mixed salt (Fig. 3a). This is consistent with the results of phase production shown in Fig. 1 and it was determined that there was higher growth of synthesized particles when KOH-KCl was used. Fig. 3a shows primary particles with a size of approximately 20 nm and the particles shown in Fig. 3b are slightly smaller. Aggregation of particles was observed in both conditions, but in the case of the reaction using KOH, the low solubility of the base materials induced more aggregation of particles compared to the reaction using KOH-KCl[7].This is consistent with the findings reported by Park *et al.*[7] that rate of dissolution according to the solubility of salt affects the shape of the particles during synthesis. In this study, sufficient verification was not conducted with respect to this result. However, a relatively satisfactory dispersion state was observed in the reaction using KOH-KCl. Thus, it was determined that using KOH-KCl was more advantageous

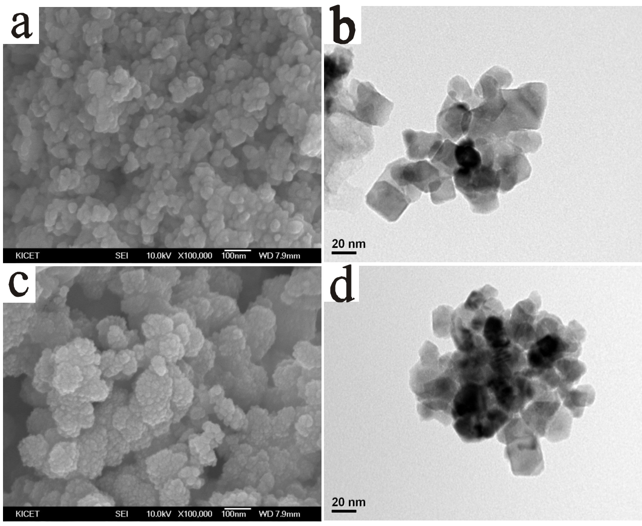

Fig. 3. SEM and TEM images of $BaTiO_3$ powders synthesized at 450 °C for 1 h with the variation of salt (a-b) KOH-KCl and (c-d) KOH

in terms of reaction rate and dispersion of particles and a decision was reached to experiment with a variety of factors using KOH-KCl for low temperature synthesis.

Fig. 4 shows the results of the XRD analysis on the nano $BaTiO_3$ particles synthesized for 10 h, according to the changes in temperature during synthesis using KOH-KCl. The liquid creation temperature of KOH-KCl is 401 °C as shown in the phase diagram of Fig. 2 and from the results of the phase analysis, it was determined that $BaTiO_3$ particles can be synthesized at 250 °C and 200 °C. Also, maintaining the reaction over the course of 10 h resulted in a synthesis peak, where there were almost no non-reactants, at 200 °C. Meanwhile, there were peaks of the non-reactant base materials, $BaCO_3$ and TiO_2, observed without a $BaTiO_3$ peak when the synthesis reaction occurred at 150 °C. In the conventional molten salt method, synthesis is known to occur due to the dissolution of base materials caused by the molten salt at temperatures higher than the melting point. However, it was inferred that there is another factor influencing the synthesis of $BaTiO_3$ and dissolution of base materials and this shows the possibility of synthesizing $BaTiO_3$ at temperatures lower than the melting point.

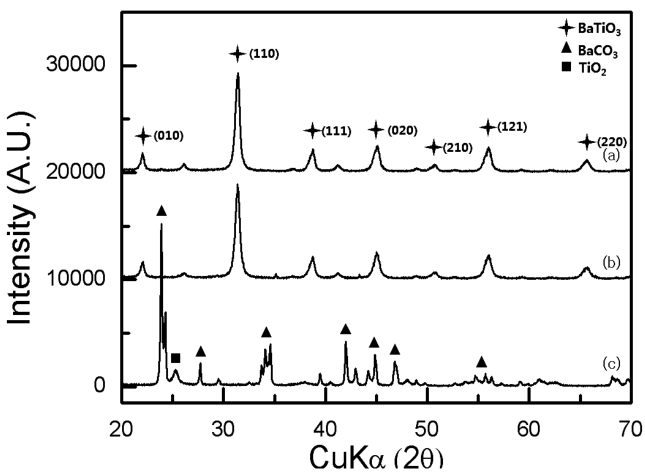

Fig. 4. XRD patterns of $BaTiO_3$ powders synthesized at (a) 250 °C, (b) 200 °C and (c)150 °C for 10 h

KOH has a strong tendency to absorb CO_2 and H_2O and produces K_2CO_3 and H_2O by reacting with CO_2. The reaction equation is $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$[8] with the characteristics of deliquescence and high solubility. Thus, it is likely to dissolve after reacting between one of the products and H_2O and produce a salt solution. It is thought that synthesis at lower temperature than the melting point is made possible through the salting-in effect.

Fig. 5 shows the results of the XRD analysis on the nano $BaTiO_3$ powder that was synthesized at 150 °C for 10 h as the concentration of KOH-KCl was changed from 1 M to 7.6 M and 15.2 M. In the case of the powder that was synthesized at high concentrations of 7.6 M and 15.2 M, a clear $BaTiO_3$ peak was observed, whereas no peak was observed when the concentration was 1 M. This is due to the increase in solubility and reaction rate caused by the salting-in effect when water is added to mixed salt[3]. As for 15.2 M, where relatively low amount of water was added, maintaining uniformity of reaction was difficult, which resulted in the peak of a non-reactant base material. The above results prove that $BaTiO_3$ was sufficiently synthesized in salt solution at 150 °C, temperature at which synthesis was deemed impossible in Fig. 4.

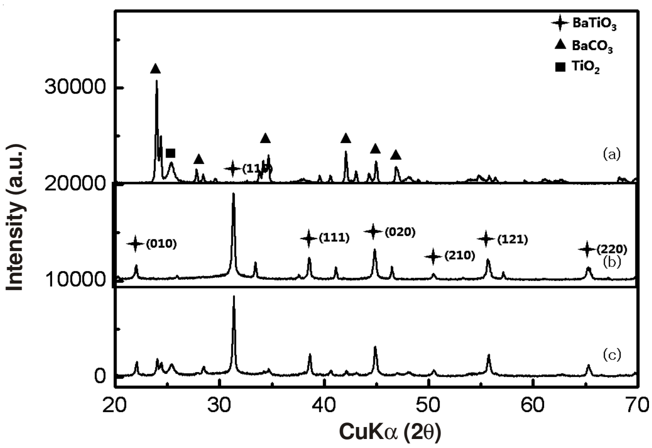

Fig. 5. XRD patterns of $BaTiO_3$ powders synthesized at 150 °C for 10 h with the concentration of salt at (a) 1 M, (b) 7.6 M and (c) 15.2 M

Fig. 6 shows the results of the XRD analysis on the $BaTiO_3$ powder that was synthesized for 1 h in KOH-KCl salt solution according to the changes in the synthesis temperature. In generally, it shows a high peak of non-reactant base material and a decrease in intensity of the $BaTiO_3$ peak from 160 °C to 120 °C. However, it also shows the main peak of $BaTiO_3$ starting at 120 °C, which proves that synthesis is possible at temperatures over 120 °C. This suggests that synthesis of $BaTiO_3$ can occur at a much lower temperature than 401 °C, the melting point of the salt, by adding water, unlike the conventional idea that synthesis is only possible at temperatures higher than the melting point of the salt used in the synthesis during the application of the molten salt technique.

Conclusion

Nano $BaTiO_3$ particles were synthesized through the molten salt technique using KOH and KOH-KCl. Using mixed salt was proven to be more advantageous compared to using single salt (KOH) as it dissolves the base materials better,

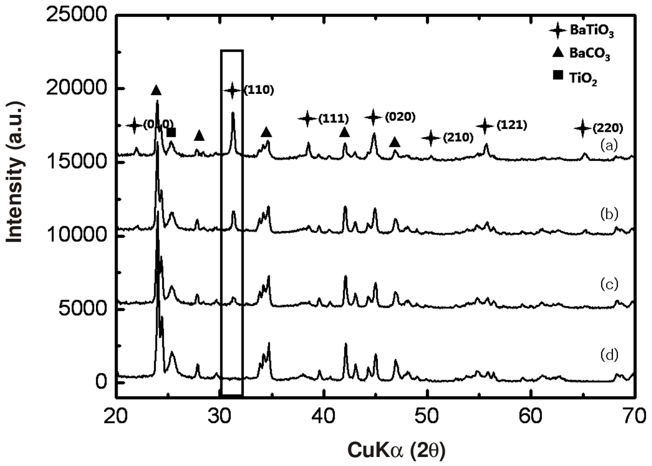

Fig. 6. XRD patterns of $BaTiO_3$ powders synthesized at (a)160 ºC, (b)140 ºC, (c)120 ºC and (d)100 ºC for 1 h with the concentration of salt at 7.6 M

facilitates the reaction and promotes the growth of particles. In the case of the mixed salt, synthesis occurred at temperatures below the melting point of the salt. The results of the low-temperature synthesis experiment where different amount of water was added showed that synthesis occurred at over 120 ºC when the salt concentration was 7.6 M. It was determined that low-temperature synthesis is possible due to the increase in solubility caused by the salting-in effect. It is expected that utilizing this phenomenon will allow synthesis of dispersed $BaTiO_3$ particles with a size of 10 nm at temperatures below 200 ºC.

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