Proceedings of Symposium on Ultrasonic Electronics, Vol. 32 (2011) pp. 297-298
8-10 November, 2011

Numerical Simulations of Sonochemical Production and Aggregation of $BaTiO_3$ Nanocrystals

超音波照射による $BaTiO_3$ ナノ粒子生成と凝集の数値シミュレーション

Kyuichi Yasui† and Kazumi Kato
(National Institute of Advanced Industrial Science and Technology (AIST))
安井 久一†, 加藤 一実 (産総研)

1. Introduction

Recently, Dang, Kato et al. [1-3] reported an ultrasound-assisted synthesis of $BaTiO_3$ nanoparticles in aqueous solutions. The reaction formula in their experiment is as follows.

$$BaCl_2+TiCl_4+6H_2O \rightarrow Ba(OH)_2+Ti(OH)_4+6HCl \quad (1a)$$
$$6HCl+6NaOH \rightarrow 6NaCl+6H_2O \quad (1b)$$
$$Ba(OH)_2+Ti(OH)_4 \rightarrow BaTiO_3+3H_2O \quad (1c)$$

Distilled water was purged with argon gas for 30 min. $BaCl_2$ was dissolved in it. After that, $TiCl_4$ was added to it, resulting in a Ti-based sol suspension. The atomic ratio of Ti to Ba was 1. Then, a 5 M NaOH aqueous solution was added to it at room temperature to make the pH 14. The suspension was irradiated with an ultrasonic horn at 20 kHz in open air for 20 min. at 80 ^oC. Then $BaTiO_3$ nanoparticles were formed. For comparison, the same reaction was performed with mechanical stirring without ultrasound. $BaTiO_3$ particles were produced only after 8 hours at the same temperature (80 ^oC). Furthermore, the particle size was 1-2 μm which is much larger than that (0.2-0.4 μm) of the sonochemically synthesized one. Another dramatic difference is the morphology of particles. Surprisingly sonochemically synthesized particles were mesocrystals which are aggregates composed of nanocrystals attached with orientation between specific crystal faces [4]. It was confirmed by the electron diffraction pattern of one whole aggregate which was quite similar to what would be observed on a single crystal [1-3]. On the other hand, particles synthesized by mechanical stirring without ultrasound were not aggregates of primary particles but large primary particles with an irregular shape. Dang et al. [1] measured the particle size distribution by the dynamic light scattering method for various initial concentrations of $BaCl_2$ (or $TiCl_4$).

† e-mail address: k.yasui@aist.go.jp

In general, the average particle size (the average size of aggregates) was larger for lower initial concentration of $BaCl_2$. The average particle sizes were 400, 150, and 100 nm for the initial concentrations of 0.05, 0.2, and 0.4 mol/L, respectively. The size of a primary particle (nuclei) was about 5 nm.

In the present paper, a theoretical model for the production and aggregation of $BaTiO_3$ nanoparticles under ultrasound has been constructed and numerical simulations have been performed based on the model.

2. Model

The production of $BaTiO_3$ particles consists of four steps. The first is the generation of $BaTiO_3$ in the liquid by the chemical reactions ((1a)-(1c)). The second is nucleation of $BaTiO_3$ nanocrystals. The third is the crystal growth. The last is the aggregation of nanocrystals.

In the present study, the crystal growth is neglected because in the experiment of Dang, Kato et al. [1-3] there were little defects in $BaTiO_3$ nanocrystals which indicate a slow crystal growth.

In the present numerical simulations, the four processes except the crystal growth have been simultaneously simulated using the following equations.

Firstly, the chemical reaction rate is discussed. Assuming the second-order reaction for the reaction (1a)-(1c), the concentration of $BaTiO_3$ in the liquid phase is given by Eq. (2).

$$[BaTiO_3]_t = c_0\left(1-\frac{1}{1+k_2c_0t}\right) \quad (2)$$

where $[BaTiO_3]_t$ is the concentration of $BaTiO_3$ in the liquid at time t neglecting the effect of nucleation of $BaTiO_3$ crystals, c_0 is the initial concentration of $BaCl_2$ (or equivalently that of $TiCl_4$), k_2 is the rate constant, and t is time (t=0 is when the reaction starts).

Secondly, the nucleation rate of $BaTiO_3$

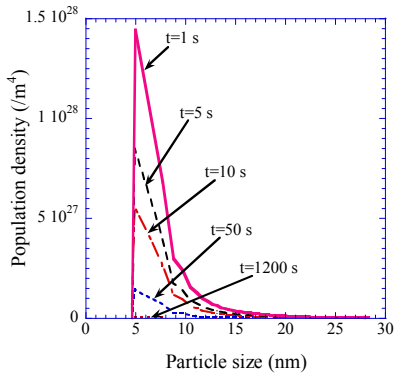
nanocrystals is discussed [5]. According to Kordylla et al. [5], the bubble surfaces act as nucleation sites because the nucleation work is decreased by the liquid/gas interfaces. Using the decreased nucleation work (ΔG^*_{het}), the nucleation rate (J) of $BaTiO_3$ nanocrystals is calculated by Eq. (3).

$$J = z \cdot k^* \cdot C_0 \exp\left(\frac{-\Delta G^*_{het}}{k_B T}\right) \qquad (3)$$

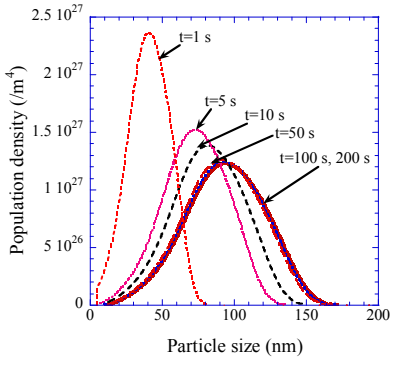
where z is the Zeldovich factor, k^* is the diffusion controlled frequency factor, and C_0 represents the number of the nucleation sites on the bubble surfaces per unit volume of the liquid.

Finally, aggregation of nanocrystals is discussed. In the present study, two models of aggregation have been considered. One is the model widely used in aerosol dynamics that any pair of particles can aggregate when they collides each other. The other is a new model that only primary particles (nuclei) aggregate with other particles. The equations for the two models have been described in Ref. [6].

3. Results and Discussions



(a)



(b)

Fig. 1 The temporal development of the particle size distribution (the results of numerical simulations). (a) The model of aggregation that any particles can aggregate. (b) Only primary particles aggregate. Reprinted from Ultrasonics Sonochemistry, vol. 18, K.Yasui, T.Tuziuti, and K.Kato, Numerical simulations of sonochemical production of $BaTiO_3$ nanoparticles, pp.1211-1217, Copyright (2011), with permission from Elsevier

The model of aggregation that only primary particles aggregate with other particles reproduces the experimentally observed particle size distribution, while the model that any particles aggregate does not.

We have also performed numerical simulations of collisions of a pair of $BaTiO_3$ nanoparticles assuming that there is electric dipole moment in the particles. When the spontaneous polarization is 5 x 10^{-4} C/m^2, only primary particles aggregate and they are oriented at the attachment. It is suggested that 5 nm $BaTiO_3$ nanocrystals synthesized with ultrasound may have spontaneous polarization.

4. Conclusion

Numerical simulations of production and aggregation of $BaTiO_3$ nanoparticles have indicated that only primary particles aggregate with other particles. Based on electric dipole-dipole interaction model for oriented attachment of $BaTiO_3$ nanocrystals, it is suggested that 5 nm $BaTiO_3$ nanocrystals may have the spontaneous polarization.

Acknowledgment

The authors would like to thank T.Tuziuti and F.Dang for their valuable comments.

References

1. F.Dang, K.Kato, H.Imai, S.Wada, H.Haneda, and M.Kuwabara: Jpn. J. Appl. Phys. **48** (2009) 09KC02.
2. F.Dang, K.Kato, H.Imai, S.Wada, H.Haneda, and M.Kuwabara: Ultrason.Sonochem. **17** (2010) 310.
3. F.Dang, K.Kato, H.Imai, S.Wada, H.Haneda, and M.Kuwabara: Cryst.Eng.Commn. **12** (2010) 3441.
4. R.Q.Song and H.Colfen: Adv.Mater. **22** (2010) 1301.
5. A.Kordylla, T.Krawczyk, F.Tumakaka, and G..Schembecker: Chem.Eng.Sci. **64** (2009) 1635.
6. K.Yasui, T.Tuziuti, and K.Kato: Ultrason.Sonochem. **18** (2011) 1211.