Preparation of $BaTiO_3$ particles by salt-assisted spray pyrolysis

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INTRODUCTION

Tetragonal barium titanate ($BaTiO_3$) is used in electronic devices for its ferroelectric properties while its cubic phase has a high dielectric constant, thus making it suitable for use in capacitors. The dielectric constant and crystal structure are dependent on the grain size of the particles. Several hours are required to produce homogeneous and highly crystalline particles using hydrothermal and mechanochemical routes. The disadvantages of these processes include inhomogeneous chemical composition, strong agglomeration, a rather poor morphology and difficulties in controlling crystal size.

Spray pyrolysis is widely known to be a continuous, single-step preparation method for the production of fine particles. Conventional spray pyrolysis (SP) results in multiple nanosized crystallites that are virtually inseparable, since they form a three dimensional network. Xia et al.[1] reported that the presence of a salt in the precursor solution drastically inhibited the agglomeration of nanocrystallites. These salts remain on the particle surface and hinder the bonding of nanocrystallites. The salts can be easily removed by washing. The SASP requires no further thermal treatment of the product, such as calcination or annealing, because the metal salts enhance the homogeneity of the crystals and crystal growth.

Optimum conditions for the synthesis of non-agglomerated $BaTiO_3$ particles by salt-assisted spray pyrolysis (SASP) were investigated. The effect of salt concentration and droplet-particle residence time in hot zone on the crystallinity, morphology and size of $BaTiO_3$ particles was examined.

EXPERIMENTAL

Precursor solutions were prepared by dissolving a stoichiometric ratio of $Ba(NO_3)_2$ and $Ti(OC_3H_7)_4$ in dilute 1 mol/l nitric acid. The concentration was set from 0.01 to 0.05 mol/l of $BaTiO_3$, while the Ba/Ti ratio of the precursor solutions was 1.00 for all experiments. Solutions of KNO_3 and $NaNO_3$ were added to the precursor solution with salt/Ti molar ratios of 0.0-50.0.

The detail of experimental setup were shown in elsewhere.[2] The precursor solution was sprayed by means of an ultrasonic aerosol atomizer into a 1.3 cm inner diameter, 150 cm length ceramic tube heated by an electric furnace at 1000°C. Nitrogen, at a flow rate of 1 l/min, was used as a carier gas. The products were collected by an electrostatic aerosol precipitator. To remove the salt, the collected particles were washed, centrifuged with water and dried.

The crystalline phases were examined by X-ray diffraction (XRD). The grain size and morphology of the particles were characterized by field emission scanning electron microscopy (FE-SEM)

RESULTS AND DISCUSSION

All SP-prepared particles show the presence of cubic $BaTiO_3$. All SASP-prepared samples have sharper peaks indicating the presence of larger crystallites than the SP sample. The amount of tetragonal $BaTiO_3$ increases with increasing salt/Ti ratios indicating that the SASP procedure not only enhances the crystallinity but also controls the phase composition through the salt/Ti ratio at the same operation temperature.

Figure 1 shows FE-SEM images of the effect of salt concentration the morphology of $BaTiO_3$ particles for a precursor solution concentration of 0.05 mol/l. The particles prepared without salt [Fig.1(a)] are spherical with a rough surface. At a higher salt/Ti ratio [Fig.1(b)], the degree of agglomeration was decreased resulting in nearly nonagglomerated, crystalline particles. By increasing the salt/Ti ratio, the agglomerated particle size tended to decrease, but the primary particle size and crystallinity of $BaTiO_3$ were increased. Decreasing the precursor concentration led to a decrease in the primary particle size and crystallinity. The degree of crystallization is affected not only by the temperature and processing time, but the solution composition and salt concentration as well.

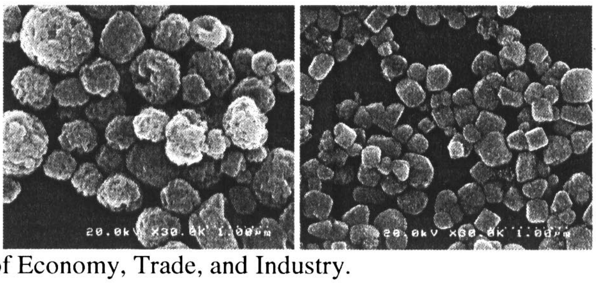
The effect of droplet/particle residence time in hot zone on the morphology of $BaTiO_3$ particles were investigated by changing the heating length or the carrier gas flow rate. By increasing the furnace length from 20 to 40 and 100 cm, the size of primary particles is increased. When the carrier gas flow rate is increased, the primary particle size decreased.

CONCLUSIONS

By increasing the salt concentration or the particle residence time in the hot zone, the primary particle size was increased and its surface texture was improved compared to $BaTiO_3$ particles, prepared by conventional spray pyrolysis. $BaTiO_3$ crystal was transformed from cubic to tetragonal by simply increasing the salt concentration at constant temperature and residence time. Further thermal treatments such as calcination or annealing are not necessary to obtain agglomerate-free tetragonal $BaTiO_3$ particles with a narrow size distribution.

AKNOWLDGEMENTS

We thank Prof. S. E. Pratsinis (ETH Zurich) and Dr. B. Xia (Univ. Minnesota) for valuable discussions. This work was supported by JSPS and NEDO/Nanotechnology Particle Project based on funds provided by the Ministry



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