SUMMARY OF Ph.D. DISSERTATION

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Title

Homogenization of starting mixture and addition of organic compounds for synthesis of high tetragonality barium titanate microparticles via a solid state route.

Abstract

To realize further miniaturization and higher capacitance of multi-layer ceramic capacitors (MLCCs), $BaTiO_3$ (BT) powders with smaller grains (<200nm), with highest possible crystallinity are required. At the same time a well-known lost of tetragonality by the reduction of BT particle size should be avoided. In general, these characteristics of BT from wet chemical methods are superior to that of BT from solid state reaction. A decisive drawback is that wet chemical methods are too costly in the mass-production. Therefore the objective of this study is to improve solid state processes of BT powder toward finer grains, narrower particle size distribution, and higher tetragonality.

The BT formation reaction was suppressed under CO_2. There are few reports for relationship between reaction process and BT particle shape and crystallinity, despite considerable research for reaction processes. Therefore the effect of CO_2 atmosphere on morphology and growth of particle of BT was examined in chapter 3.

Ceramic powders are usually dispersed with a ball mill or media agitation mill. Mechanical stressing induces the mechanochemical effect. Mechanochemcal effects are quite effective for acceleration of the solid state reaction. The effects of dispersion treatment on starting materials, BT formation reaction, BT particle morphology and crystallinity were investigated in chapter 4~6. Higher mixing homogeneity of the starting mixture and mechanochemical effects by the dispersion treatments of $BaCO_3$ and TiO_2 brought the BT formation of smaller particles and narrower particle size distribution. Furthermore, the organic compounds such as amino acid or polyamide which have -C=O groups and >NH- groups as well as the abraded nylon by dry ball mill treatment accelerated decarboxylation of $BaCO_3$. However, in chapter 6, the extremely active surface of the starting mixture by strong mechanochemical effects accelerated not only the BT synthesis reaction but also BT particle growth in the reaction process simultaneously. The ultra-fine starting materials with higher mixing homogeneity without strong mechanical activation result in BT particles with finer and narrower size distribution and higher tetragonality.

Considering mass production, ultra-fine materials have many problems on the cost and handling ability. And the wet dispersion process is superior to the dry process due to high throughput at present. Therefore, the effect of addition of glycine to the mass production conscious fine starting materials on the wet dispersion process was examined. Role of glycine was manifold including enhancing thermal decomposition of $BaCO_3$ and, upon higher loading, adsorption to TiO_2 and destabilize TiO_6 units to assist diffusion of Ba^{2+} ion.

The acceleration of the reaction for addition of organic compounds was applied for the BT formation of smaller particle and higher tetragonality, in chapter 8.

Consequently, decreasing reaction temperature or forming of BT nuclei at one time everywhere and suppression of BT grain growth resulted in the synthesis of BT with smaller particles, narrower particle size distribution and higher tetragonality.