Effect of Calcination Temperature on Phase Transformation and Particle size of Barium Titanate Fine Powders Synthesized by the Catecholate Process

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Abstract   A modified catecholate process has been developed for the synthesis of high purity barium titanate fine powders. The barium titanium-catechol complex, $Ba[Ti(C_6H_4O_2)_3]$ was prepared from $TiCl_4$, $C_6H_4(OH)_2$ and $BaCO_3$. The complex was freeze-dried and calcined for 3 hours at temperatures ranging from 700 to 1100°C. Phase transformation and particle size of the calcined powders have been investigated as a function of calcination temperature by room-temperature X-ray diffraction and scanning electron microscopy techniques. It is seen that the perovskite-like phase of $BaTiO_3$ was successfully obtained. With increasing calcining temperature, $BaTiO_3$ transformed from the cubic to the tetragonal phase. Higher temperatures clearly favoured particle growth and the formation of large and hard agglomerates. After calcination at 700°C, the average particle size ranged between 0.1-0.2 μm.

KEYWORDS: barium titanate, phase transformation, catecholate process.

INTRODUCTION

This study is the continuation of our current efforts[1,2] to develop a new synthetic route for the preparation of fine barium titanate powder and to examine the effect of calcination temperature on phase transformation and particle size of the final products.

Barium titanate is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multi-layer capacitors (MLCs), PTC thermistors, piezo-electric transducers and a variety of electro-optic devices.[3-7] Conventionally, barium titanate has been synthesized by a solid-state reaction between $BaCO_3$ and TiO_2.[8-10] The overall reaction involves the initial formation of $BaTiO_3$ at $BaCO_3/TiO_2$ grain boundaries which then reacts with $BaCO_3$ resulting in the formation of Ba_2TiO_4. Finally, $BaTiO_3$ was obtained from the reaction between Ba_2TiO_4 and TiO_2 under optimum conditions. During this reaction, precise control of stoichiometry and powder characteristics are difficult to maintain because of lack of consistency in raw material sources and local inhomogeneities arising from incomplete mixing and reaction of the constituents. The high calcination temperatures needed for this reaction to occur often result in the formation of coarse aggregates which can be difficult to disperse or reduce during subsequent milling. To overcome these deficiencies, alternative methods of powder synthesis have been developed and described by many authors such as co-precipitation of oxalates,[11-13] citrates,[14-16] catecholate[17-19] and others.[20-25] Most of these techniques take advantage of reactions that favour the homogeneous distribution of barium and titanium on an almost atomic scale in solution so that the same distribution is largely maintained also in the precipitates. The immediately adjacent ions of barium and titanium can therefore react with each other at relatively low temperatures to form homogeneous and stoichiometric barium titanate.

It is well known that the physical properties of ceramics are very sensitive to their microstructure. Hence, it is essential to control the properties of the initial barium titanate powder in order to produce ceramics with dense, uniform and fine-grained microstructure.[26,27] Carbone and Reed[28] have shown that the particle size distribution and agglomerate structure of the starting powders have an important influence on the microstructure achieved in $BaTiO_3$. It is necessary to control the particle size distribution and the precise composition in the powder in order to obtain dense sintered ceramics with uniform grain size of particle morphology. The catecholate technique

first proposed by Ali and Milne[17] is one of the few techniques which are able to deliver a particle size in the range of nanometers and offer the possibilities of close control of the homogeneity and purity of the powders. It has been successfully used to prepare a range of fine powders, including perovskite compounds.[18,19] Only an organic complexing agent (the catechol) will be utilized to form a complex which is readily decomposed to crystalline product by heating. In this paper, we focus on the effect of the calcining temperature on phase composition and microstructural evolution of barium titanate fine powders synthesized by the catecholate process.

MATERIALS AND METHODS

Sample preparation

The modified catecholate process[17] for barium titanate is shown in Fig 1. Catechol, (1, 2-dihydroxybenzene, $C_6H_4(OH)_2$) was added to dry toluene and heated to boiling to dissolve the catechol reagent. A solution of $TiCl_4$ in toluene was then added dropwise. The dark red precipitate formed was

Fig 1. Flow chart for a modified catechol- based synthesis of $BaTiO_3$ powder.

isolated by filtration. The $H_2[Ti(C_6H_4O_2)_3]$ precipitate was then gradually added to a boiling suspension of $BaCO_3$. The catecholate complex, $Ba[Ti(C_6H_4O_2)_3]$ was obtained as an aqueous solution which was freeze-dried and calcined for 3 hours at temperatures between 700 to 1100°C.

Sample characterization

X-ray diffractometry (XRD, D 5000, Crystal Structure Limited (CSL)) using CuK_α radiation was used to determine the lattice parameters and phase formation. The (002) and (200) diffraction peaks of the barium titanate powders were adopted to evaluate the crystal phase.

Scanning electron microscopy (SEM, JSM-840A, JEOL Co, Tokyo, Japan) was employed to observe the morphology and the particle size of the powders. A gold layer was coated onto the sample's surface for the SEM investigation.

RESULTS AND DISCUSSION

Powder characterization

Phase Transformation

Figure 2 shows the room-temperature X-ray diffraction patterns of $BaTiO_3$ derived from a catechol precursor complex after heat treatment for 3 hours at (a) 700°C, (b) 900°C and (c) 1100°C, with the corresponding JCPDS patterns. The strongest reflections apparent in the majority of the XRD pattern indicate the formation of high purity barium titanate, $BaTiO_3$.

Figure 3 shows the X-ray diffraction peaks of $BaTiO_3$ around $2\theta = 45°$. Sample (a) was calcined at a temperature of 700°C and shows only one symmetric (200) peak, confirming its cubic symmetry. However, samples (b) and (c), calcined at temperatures of 900 °C and 1100°C, respectively show (002)/(200) peak splitting of the diffraction lines around 2θ of 45°, pointing to an additional tetragonal phase. The intensity ratios of the modelled peaks were compared to the values given in the JCPDS files (file numbers 31-174 and 5-626 for cubic and tetragonal $BaTiO_3$, respectively). There are two phases of $BaTiO_3$, ferroelectric tetragonal phase and paraelectric cubic phase. The lattice parameters are given as a_o= 3.994 Å and c_o = 4.038 Å for tetragonal form and a_o = 4.031 Å for cubic form.[29] In our experiment, the lattice parameters calculated from the diffraction data indicate that the c/a ratios are 1.0065 (a_o = 3.992 Å, c_o= 4.018 Å at 900°C) and 1.010 (a_o = 3.992 Å, c_o = 4.030 Å at 1100°C) for tetragonal phase, and a_o = 4.01 Å for cubic phase.
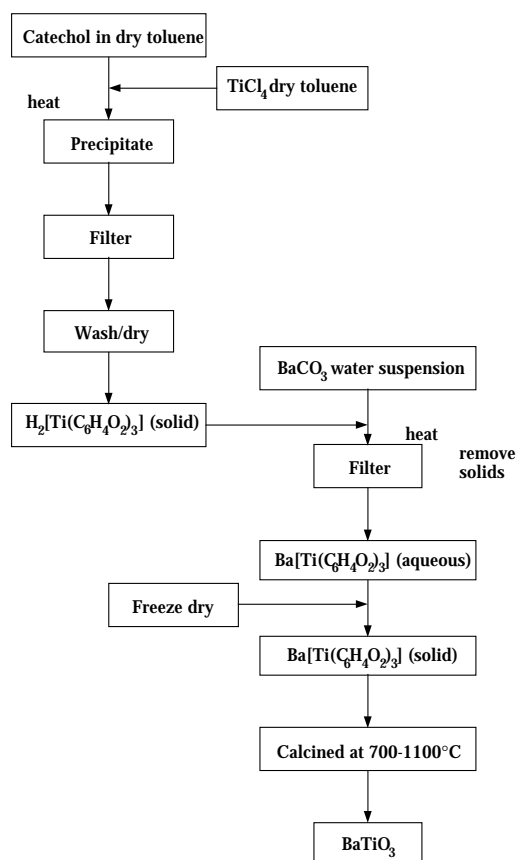
From the room temperature XRD data, it may be concluded that low calcination temperature (700°C) results in a cubic phase, in good agreement with those observed by other workers.[30,31] This metastable form can be converted to the stable tetragonal form by calcination at higher temperatures (900 and 1100 °C).

Particle size analysis

SEM micrographs of $BaTiO_3$ powders calcined at different temperatures are shown in Figure 4. Sample (a) consists of well dispersed spherical particles of reasonably uniform sizes of 0.2 μm corresponding to the cubic form, while sample (b) exhibits irregularly shaped particles. There is evidence for exaggerated grain growth, with the development of interparticle necks and consequent particle fusion, and also for an increase in particle size corresponding to pseudocubic form. In contrast to this, sample (c) clearly shows the presence of agglomerates and various sizes of clusters

and acircular shapes (tetragonal form). Moreover, it was found that the relative amount of $BaTiO_3$ in cubic form gradually decreases with the increase in particle size.

Particle size dependence of the tetragonal deformation (defined as the ratio of the lattice constant, $(c/a-1)$) between 0.5 and 1.5 μm in diameter for $BaTiO_3$ has been reported by Arlt et al.[32] Below 0.5 μm, the existence of the pseudocubic or even the cubic phase has been suggested in good agreement with this work. Because of the line broadening at the small particle size region, it is difficult to identify the cubic phase. Nevertheless, a careful analysis of
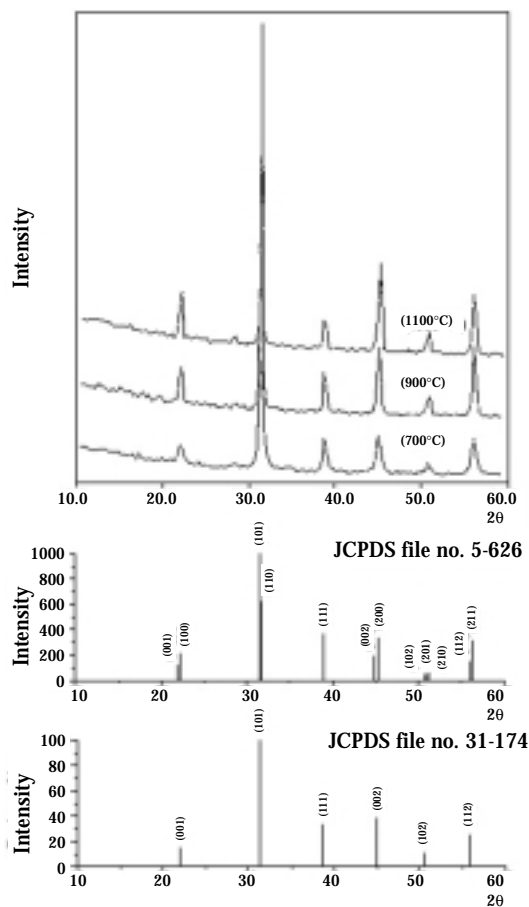

Fig 2. Room-temperature XRD patterns of the calcined powder at various calcination temperatures with constant dwell time and the JCPDS patterns for tetragonal and cubic $BaTiO_3$.
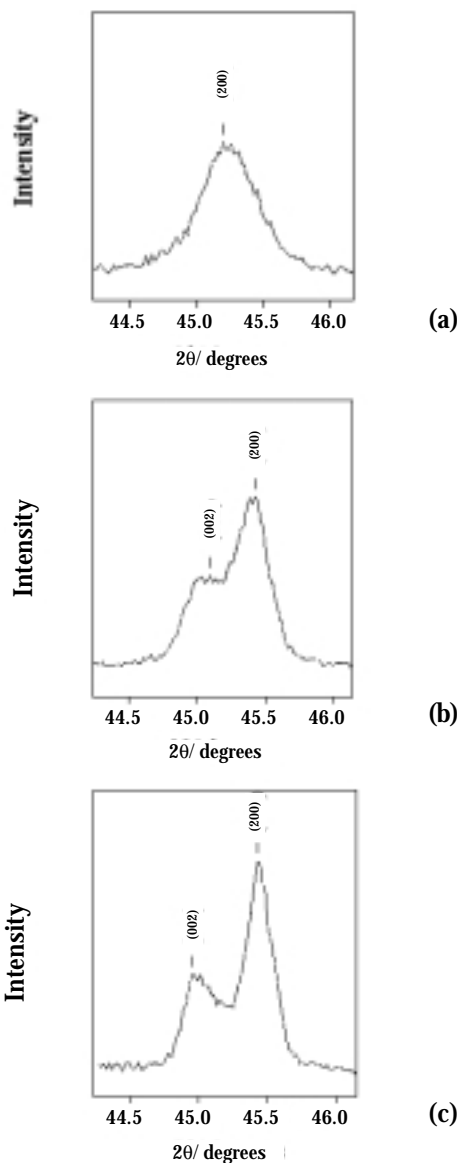

Fig 3. XRD peaks for the (002) and (200) reflections of $BaTiO_3$ powder as a function of calcination temperature (a) 700°C, (b) 900°C and (c) 1100°C.

the diffraction pattern at large angles leads to the identification of both cubic and tetragonal phases.

CONCLUSION

A modified, catecholate process for preparing high purity $BaTiO_3$ fine powders has been developed which shows a high level of reproducibility. By using a combination of room-temperature XRD and SEM techniques, the effect of the calcination temperature on phase transformation and particle size of $BaTiO_3$ was examined. The firing temperature has been found to have a pronounced effect on the formation of $BaTiO_3$ and its particle size. The cubic phase with

(a)

(b)

(c)

Fig 4. SEM micrographs of $BaTiO_3$ powder calcined for 3 hours at (a) 700°C, (b) 900°C and (c) 1100°C.

equisized, spherical and well-dispersed particles was observed at low temperature while the tetragonal phase with various sizes of clusters and hard agglomerates was found at high temperature.

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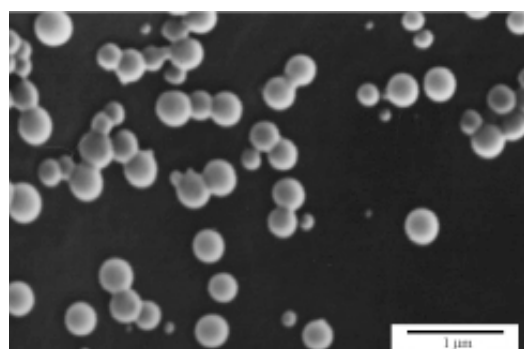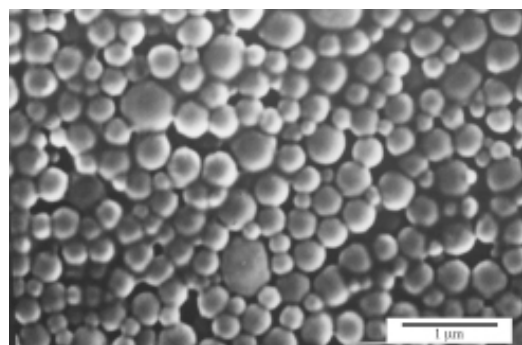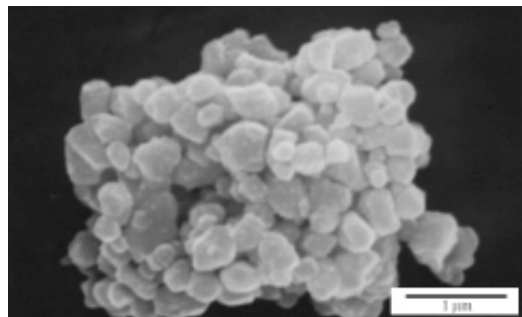
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