Change from Metastable Cubic to Stable Tetragonal Form of Submicron Barium Titanate

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The change from metastable cubic to stable tetragonal form was investigated on the submicron $BaTiO_3$ which was prepared by the hydrolysis of titanium tetraisopropoxide in barium hydroxide solution and by crystallization in the glass of $BaO–TiO_2–SiO_2–Al_2O_3$ system. The precipitated $BaTiO_3$ was found to be the aggregates of minute grains of about 100 Å, to have large amount of strain and to absorb about 6% of OH and alcoholic radicals, some of them absorbed chemically. It is in a metastable cubic form. After the heating above 800 °C, it changed to stable tetragonal form in association with weight loss and decrease in lattice strain. The samples heated at 800—900 °C did not show the Curie point on the DTA curve although they were tetragonal. The samples heated at 1300 °C had the Curie point about 122 °C. The glass-devitrified $BaTiO_3$ was also cubic and had large lattice strain. In order to change to tetragonal form, the heating above 1000 °C was needed. The metastable cubic form of submicron $BaTiO_3$ seemed to be stabilized by the absorbants on the surface which balanced with large amount of strain in the lattice.

As the raw materials for the preparation of high-density sintered ceramic bodies, as the catalysts and as the filler materials, high-purity submicron oxide powders have been studied. On these oxide powders, some structural anomalies have been observed. For example, ZrO_2 prepared from zirconium tetra-tertiary butoxide by thermal decomposition was found to have cubic form,[1] and that precipitated from alkaline aqueous solution and calcined at low temperature was tetragonal,[2] although the monoclinic form was stable at room temperature. $BaTiO_3$, of which stable form at room temperature was tetragonal, was cubic when it was prepared by pyrolysis of barium titanyl oxalate or by simultaneous hydrolysis of barium bis-isopropoxide and titanium tetrakis-tertiary amyloxide.[3,4] The appearance of these metastable forms of oxides were discussed mainly in relation to their small crystallite sizes.

On the $BaTiO_3$ ceramics, the dependence of dielectric constant on particle size has been studied in detail. The ceramics with fine particle size of about 1 μ was found to have very different temperature dependence of dielectric constant from that with coarse particles (about 50 μ), the latter having a similar behavior to the single crystal, and the former showing very diffuse transition from tetragonal to cubic form and having large dielectric constant at room temperature.[5,6] The maximum of dielectric constant at the particle size of about 1 μ was reported on the $BaTiO_3$ which was crystallized in the glass.[7] The decrease of dielectric constant with the decrease of particle size was also shown on the pure, unsintered and pressed $BaTiO_3$.[8] These experimental results were discussed on the basis of internal strain of the crystallite, many faults in the lattice or nonferroelectric surface layer of the particle.

In the present work, the change of $BaTiO_3$ from the metastable cubic to the stable tetragonal form was investigated, in relation to lattice strain, on the submicron $BaTiO_3$ powders.

Experimental

Preparation of Submicron $BaTiO_3$ Powder. The submicron $BaTiO_3$ powders were prepared in the same way as Kiss *et al.*[3] In the 0.41—0.48 N aqueous solution of barium hydroxide (reagent grade) with pH of 11—13, the isopropyl-alcohol solution of the equivalent molar weight of titanium tetra-isopropoxide (CP grade) was hydrolyzed and the precipitates were obtained. During the reaction, the solution was stirred violently and kept at 90 °C in the N_2 atmosphere. After aging the precipitates in the solution at 90 °C, it was filtered, washed by water and then dried in a vacuum. The stoichiometry of the prepared samples was known by the fact that any additional phases, such as Ba_2TiO_4, $BaTi_2O_5$, and TiO_2, were not identified by X-ray after the heating at 1100 °C. The non-stoichiometry of the precipitates occurred from the lowering of pH during the reaction could be avoided by the addition of KOH in the $Ba(OH)_2$ solution to keep the pH-value constant.

The samples thus prepared were heated at various temperatures from 120 °C to 1300 °C in air and studied by X-ray diffraction techniques, electron microscopy, thermal analyses (DTA and TGA), and infrared absorption spectra.

Crystallization of $BaTiO_3$ in the Glass. The crystallization of $BaTiO_3$ in the glass was performed according to Herczog.[7] The glass was prepared from the mixture of 42.9 mol% $BaCO_3$, 35.8% TiO_2, 14.2% SiO_2, and 7.1% Al_2O_3 by melting at 1480 °C for 2 hr, after 1200 °C pre-heating, in the platinum crucible and quenched into water.

The glass samples thus prepared were heated at 800 °—1200 °C in air and the precipitated microcrystalline $BaTiO_3$ was studied by X-ray.

Results and Discussion

X-Ray Diffraction Studies. X-Ray diffraction patterns of submicron $BaTiO_3$ are shown in Fig. 1. After heating at 120 °C for 24 hr, X-ray pattern of the sample is indexed by the cubic system, which have to be the high-temperature modification of $BaTiO_3$. After heating at 1300 °C for 5 hr, however, the sample is tetragonal, of which X-ray pattern is not differentiated from the crystal prepared by solid state reaction.

In the $BaO–TiO_2–SiO_2–Al_2O_3$ system glass, $BaTiO_3$ crystals were precipitated by the heating above 800 °C. The crystals precipitated after heating at 800 °C for 5 hr were also cubic and those after heating at 1200 °C were tetragonal, which coexisted with small amount of hexagonal feldspar $BaAl_2Si_2O_8$.

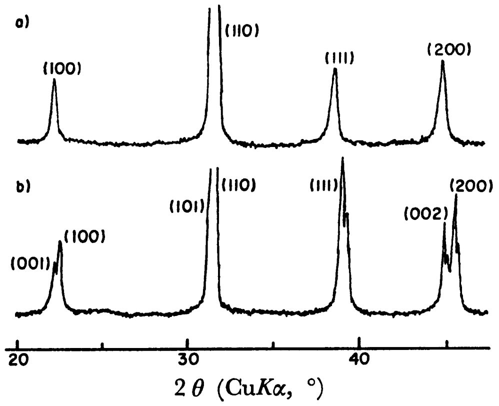

Fig. 1. X-ray diffraction patterns of submicron $BaTiO_3$ heated at 120 °C for 24 hr (a) and at 1300 °C for 5 hr (b)

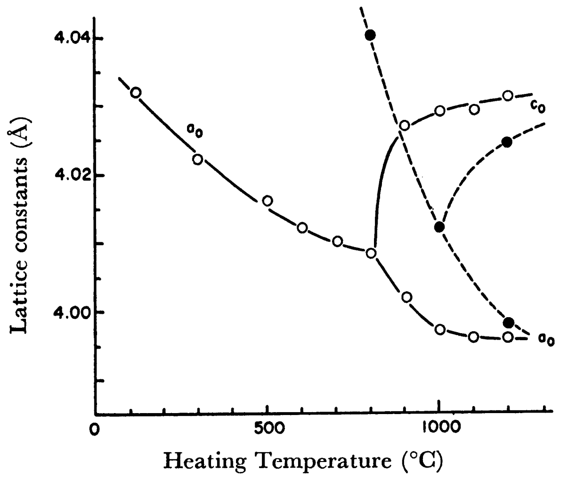

Fig. 2. Changes of lattice constants a_0 and c_0 with heating temperature for the constant heating time of 5 hr ○: precipitated, ●: glass-devitrified

On both precipitated and glass-devitrified $BaTiO_3$ samples, the changes of lattice constants a_0 and c_0, which are determined by using (111), (002), and (200) diffraction lines, with heating temperature are shown in Fig. 2. The transition temperature from the metastable cubic to the stable tetragonal form is at about 800 °C for the precipitated sample and at about 1000 °C for the glass-devitrified. At low heating temperature, the unit cell of the samples is relatively large. This might suggest the existence of large amounts and many kinds of lattice defects.

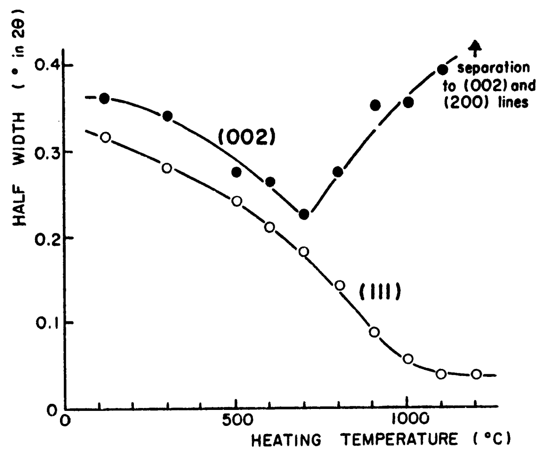

Fig. 3. Changes of half width of (111) and (002) diffraction lines with heating temperature for the constant heating time of 5 hr.

In Fig. 3, the half widths of (111) and (002) diffraction line profiles are plotted as a function of heating temperature on the precipitated $BaTiO_3$ heated at each temperature for 5 hr. The half width of (111) line decreases with the increase in heating temperature and this corresponds to the crystallite growth and the decrease in strain. However, the observed half width of (002) line shows an increase above 700 °C. This is caused from splitting of the cubic (002) line to the tetragonal (002) and (200) lines and shows consistency with the changes of lattice constants.

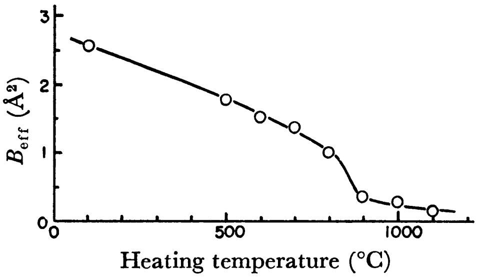

Fig. 4. Change of effective Debye parameter B_{eff} with heating temperature for the constant heating time of 5 hr.

On the same precipitated samples, the effective Debye parameter B_{eff} was measured, which was a measure of lattice strain in the powders.[9] The change of B_{eff} with heating temperature is shown in Fig. 4. With the increase of heating temperature, the value of B_{eff}, that is, lattice strain, decreases rapidly. The step-wise decrease between 800 and 900 °C corresponds to the structural change from cubic to tetragonal form.

On the metastable cubic $BaTiO_3$ devitrified in the glass, large value of B_{eff}, that is, large amount of lattice strain, was observed.

Electron Microscopic Observations. The precipitates heated at 120 °C for 24 hr, consisted of the polyhedral

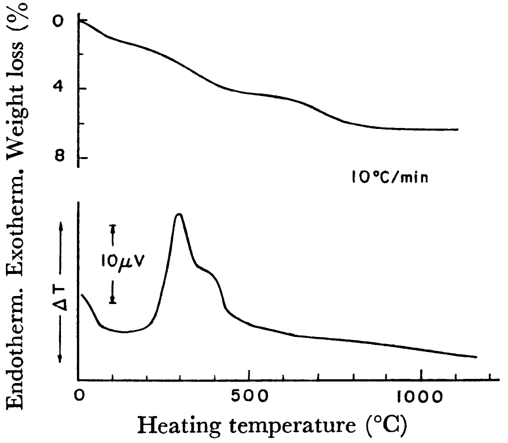

Fig. 5. TGA and DTA curves for the precipitated $BaTiO_3$.

particles with the apparent dimension of about 500 Å and these polyhedra seemed to be the aggregates of minute grains of about 100 Å. These particles grew up with the increase in heating temperature, to 0.1—1 μ in dimension after the heating at 1100 °C for 5 hr.

Thermal Analysis Studies. The results of thermogravimetric and differential thermal analyses (TGA and DTA) are shown in Fig. 5 on the precipitates heated at 120 °C for 24 hr. At 290 and 375 °C, two exothermic peaks are observed on the DTA curve. However, the weight loss occurs in two steps, though very diffuse, up to about 450 °C and to about 800 °C. The first step of weight loss corresponds to the exothermic peaks. The chemical species which cause the weight loss are supposed to be the absorbed OH and isopropoxy groups from the infrared absorption spectra for the samples quenched from different temperatures. Most of the absorbants which have been absorbed on the surfaces of submicron $BaTiO_3$ particles during their preparation, are desorbed up to 450 °C and are responsible to the exothermic peaks. Some of the absorbants remained above 450 °C and desorbed gradually up to about 800 °C. The experimental fact that one of the absorbants on the $BaTiO_3$ surfaces is OH groups, may be due to the basic nature of barium.[10]

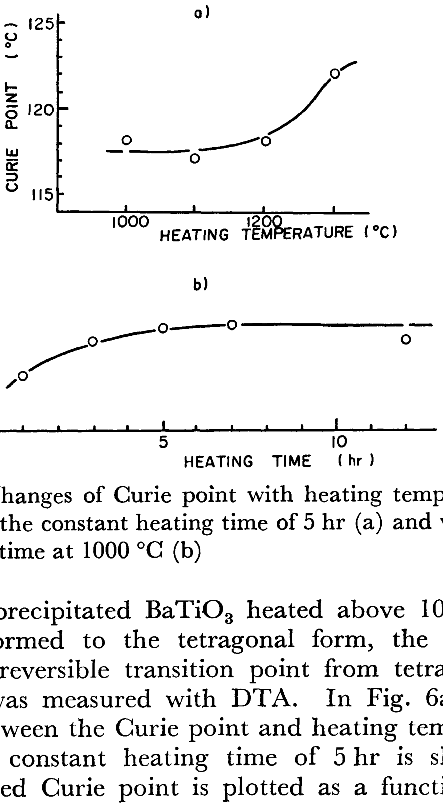

Fig. 6. Changes of Curie point with heating temperature for the constant heating time of 5 hr (a) and with heating time at 1000 °C (b)

On the precipitated $BaTiO_3$ heated above 1000 °C and transformed to the tetragonal form, the Curie point, the reversible transition point from tetragonal to cubic, was measured with DTA. In Fig. 6a, the relation between the Curie point and heating temperature for a constant heating time of 5 hr is shown. The observed Curie point is plotted as a function of heating time at 1000 °C, in Fig. 6b. With the increase of heating temperature, the Curie point increases to 122 °C. This Curie point corresponds to the value of 123 °C for the $BaTiO_3$ ceramics with coarse grain (—100 μ) reported by Jonker.[5] At 1000 °C, however, the lattice strain in the precipitates seems not to be annealed out and consequently the Curie point observed is about 118 °C even after the annealing for 12 hr. The sample heated at 900 °C was tetragonal, but Curie point was difficult to be detected on their DTA curves.

On the precipitated $BaTiO_3$ heated below 900 °C, the Curie point was not detected at low temperatures down to the liquid nitrogen temperature. This fact suggests that the Curie point disappears, not shifts to low temperatures, probably because of the presence of strain.

The measurement of dielectric constant was carried out on the pressed specimens of the precipitated $BaTiO_3$. However, the reliable value of dielectric constant was difficult to obtain because of the lack of the sufficiently dense specimens.

On the Formation of Metastable Cubic Form. The submicron $BaTiO_3$, precipitated from titanium-alkoxide and barium hydroxide solution, and precipitated in the glass matrix, had the cubic form which was metastable thermodynamically. This metastable cubic form changed to the stable tetragonal form only after heating above 800 °C for the precipitated and above 1000 °C for the glass-devitrified $BaTiO_3$. The latter needed higher temperature than the former, which might be caused from the clamping effect[11] of glass matrix. The decrease of lattice strain with heating corresponded to the change from the metastable cubic to the stable tetragonal form. Phenomenological similarity was found between the present results and the irradiation-induced transition,[12] in which the introduction of defects by irradiation resulted in the change from the tetragonal to cubic form. An amount of lattice strain remained in the tetragonal submicron $BaTiO_3$ and it caused the disappearance of the Curie point. The Curie point of $BaTiO_3$ was reported to be smeared out by grinding and compression[13] and also to disappear by the irradiation in the amount of 2.1×10^{20} nvt.[14]

As shown in the TGA and DTA curves, the submicron precipitates absorbed OH and isopropoxy groups on their surfaces, some amount of radicals being absorbed chemically. The space charge layer, which has been supposed to be present on the surface of ferroelectric solids,[15] did not appeared to exist in the present submicron $BaTiO_3$ because the charges, if they existed, might be diverged or cancelled out by the absorption of OH and alcoholic radicals. The cubic form was assumed to be stabilized, though metastably, by the absorbants which might balance with large strain in the metastable lattice structure. Above 800 °C at which almost all absorbants disappear, the submicron $BaTiO_3$ transformed to tetragonal form. On ZrO_2, the tetragonal form (hightemperature form) has been known to appear metastably at room temperature by bonding the small amounts of OH groups.[16]

The large lattice strain of the metastable cubic form of $BaTiO_3$ seemed to be related to the small particle size. According to Goswami,[8] the strained surface layer of $BaTiO_3$ particles is non-ferroelectric. The particle size of the present submicron $BaTiO_3$ is much smaller than the reported values of surface layer thickness.[8] In other words, all of the submicron particles have the characteristics of the surface layer, large strain and non-ferroelectric.

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