Microstructural Observations of Cu₂O-Added BaTiO₃ Sintered under N₂ Flow

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1. Introduction
Effects of dispersion of metallic phase into ferroelectric materials have been examined for various combinations, such as PZT/Ag,¹ PZT/Pt,² and BaTiO₃/NP³ systems. A small amount of metallic phase dispersed into ferroelectric ceramics has been known to improve the mechanical properties such as flexural strength and fatigue without degrading the electrical properties. The dispersed metallic phase can act as a bridge against crack propagation and increase fracture toughness and strength of the matrix. The advantage of dispersing metallic phase into ferroelectric ceramics is evident not only in the mechanical properties, but also in the electrical properties. The dispersed metallic phase increases the effective electrical field applied to the ferroelectric matrix while it also enhances dielectric properties.⁴,⁵ Also, silver metal in the PZT/Ag system was reported to improve PZT sinterability.⁶ In the case of the BaTiO₃/Cu system, some difficulties in dispersion of metal into ceramics during sintering are expected. Since melting points or eutectic points of the Cu–O system are known to be 1065°C, far lower than the sintering temperature of BaTiO₃, Cu metal becomes the liquid phase during sintering. Hennings et al.⁷ reported that TiO₂-excess BaTiO₃ sintering formed the eutectic melt and gave rise to pronounced discontinuous grain growth, that is, abnormal grain growth of BaTiO₃. In the BaTiO₃/Cu system, abnormal grain growth might occur due to the formation of copper liquid. There have been some limited reports on the effects of copper oxide addition to BaTiO₃ on the sintering behavior and dielectric properties of the BaTiO₃–CuO system.⁸–¹³ However, few investigations have explored microstructural observation or dispersion of Cu into BaTiO₃. In our previous work,¹⁰ reduction of Cu₂O to Cu in BaTiO₃ under 100 ml/min nitrogen flow was identified by XRD analysis; also, BaTiO₃/Cu composite was successfully fabricated by sintering under nitrogen flow. In this study, microstructural evolutions of BaTiO₃ were investigated during the fabrication of BaTiO₃/Cu by sintering Cu₂O-added BaTiO₃ in a nitrogen atmosphere. The formation mechanism of abnormal grains as well as microstructural characteristics of the present composite will be discussed in relation to Cu₂O addition.

2. Experimental procedure
Cuprous oxide (Cu₂O, high purity chemical, 99%, about 3μm) was mixed with BaTiO₃ powder (Sakai Chemical, hydrothermally synthesized powder, about 1μm) by using wet ball milling in ethanol for 24 h. The powder mixture in ethanol was dried in an evaporator, pulverized, and then sieved with a 150μm mesh. Contents of Cu₂O varied from 0 to 5mass%. Mixed powders were compacted by a stainless steel mold with 10 MPa followed by cold-isostatic pressing (CIP) at 200 MPa for 3 min to fabricate a 10 mm diameter and 3 mm thick green mass. Sintering was conducted between 1200 and 1350°C at various nitrogen gas flow rates of which the heating and cooling rates were fixed to be 20°C/min. During sintering, oxygen partial pressure was measured to reflect the thermodynamic behavior of BaTiO₃–CuO sintering.

Dispersion of copper metal in BaTiO₃ matrix was observed using an optical microscope; size distribution and area ratio of the Cu to the matrix were analyzed using the Scion image analysis program. The BaTiO₃–Cu₂O system microstructure was observed by FE-SEM (Model S-5500, Hitachi, Ltd., Tokyo) and TEM (H-8100T, 200kV, Hitachi Ltd., Tokyo). The specimen for SEM observation was ground to about 1 mm thickness, polished with 0.5μm alumina paste and then chemically etched in 5% HCl solution. The fracture surface was also observed. Constituent analysis of crystal phases was conducted by energy dispersive X-ray analysis (EDX; Horiba, Tokyo); electron probe micro-analysis (EPMA; JXA-8800R, JEOL, Osaka) was also undertaken to identify compositional distribution in the sintered specimen.

3. Results and discussion
3.1 Dispersion and size distribution of copper
Dispersed copper images of 1 and 5 mass% Cu₂O-added BaTiO₃, sintered at 1280°C for 3 h under 100 ml/min N₂ flow, are shown in Fig. 1. Copper was dispersed homogeneously in barium titanate matrix and the phase of dispersed particles was identified as copper as in our previous report.¹⁰ The remaining copper content was evaluated indirectly by analyzing the area ratio of copper to the matrix. It increased from 0.2%, for the 0.5 mass% Cu₂O addition, and to 2.3% for the 5 mass% Cu₂O addition (Table 1).

3.2 SEM observation and EDX analysis
Microstructures of the chemically etched surface (in 5 mol% of HCl) of samples sintered at 1250°C in 200 ml/
min N₂ gas flow were observed by SEM (Fig. 2). Grain size of BaTiO₃ was about 1 μm and grain growth of BaTiO₃ was not observed. However, in the 1 mass% Cu₂O-added BaTiO₃ sintered at 1280°C under 100 ml/min N₂ flow, abnormal grain growth was clearly observed as shown in Fig. 3(a). The abnormal grain size was between 50 and 70 μm. When one abnormal grain was observed by magnification, it clearly contained small particles; some of those were identified as copper by EDX analysis in Fig. 3(c) while the others were not copper. The latter were identified as barium titanate by EDX analysis and were thought to be the same as the BaTiO₃ crystalline sphere in Fig. 3. A darker contrasted region around the copper particle was also observed in Fig. 3(d), which was thought to be the diffusion layer of copper.

Abnormal grain growth is generally known to occur when particle shape is angular in liquid phase sintering. This implies that abnormal grain growth could be observed when particle growth or dissolution is controlled by the interface reaction. Different sizes of angular-shaped particles in the liquid phase need a force more than the critical driving force, ΔGc, to grow abnormally. That value is calculated as

\[
\Delta G_c \leq 2\gamma V_m \left( \frac{1}{a^*} - \frac{1}{a} \right)
\]

where \(a\) is the particle radius, \(a^*\) is critical radius, \(\gamma\) is surface energy of a particle, and \(V_m\) represents particle molar volume. Because only grains with a force greater than the critical driving force can grow, \(a^*\) must be smaller than a certain value and \(a\) must be larger than \(a^*\). In this case, large
Microstructural Observations of Cu$_2$O-Added BaTiO$_3$ Sintered under N$_2$ Flow

Grains having a force more than $\Delta G_0$ grow selectively, but other smaller grains can dissolve and disappear. As a result of DTA and TG analysis in our previous report, melts of BaTiO$_3$-Cu or BaTiO$_3$-Cu$_2$O were found to appear between 900 and 1040°C, which was consistent with the result in BaTiO$_3$-CuO sintering in air by Yang. It is expected that the copper liquid phase or the eutectic melt would play an important role in densification and abnormal grain growth, or dissolution of particles. It is not certain, however, whether abnormal grain growth began to appear at 1280°C, higher than the 1040°C considered as the eutectic melting point.

Figure 4 shows the fracture surface of 1 mass% Cu$_2$O-added BaTiO$_3$ containing a number of BaTiO$_3$ crystals whose sizes vary from hundreds of nanometers to about 10 µm. And abnormal grains began to appear in the sintered sample at 1280°C under 100 ml/min N$_2$ flow, which contained polygonal and spheroidal crystals of BaTiO$_3$. Spheroidal crystals were also observed in areas where abnormal grains were extracted, that is, in the grain boundary of abnormal grains (Figs. 4(c) and 4(d)). Spheroidal crystals are considered to have formed from several grains fusing together, as seen in Fig. 4(d). When the sample was sintered at 1350°C under 100 ml/min N$_2$ flow, the number of abnormal grains increased and the abnormal grains were filled with many spheroidal crystals of a few microns to 10 microns in size as shown in Figs. 4(e) and 4(f). Figure 5 shows crystal spheres within abnormal grains of barium titanate and the EDX analysis result for 5 mass% Cu$_2$O-added BaTiO$_3$ sintered at 1350°C. Several spheroidal crystals were observed with copper attached to the surface; also, crystal growth planes were observed on the sphere surface. In EDX analysis, the spheroidal crystal had almost identical constituents of barium and titanium as that of the matrix, but it contained small amounts of copper as evident in Fig. 5(c). The attached crystal on the surface of the spheroidal crystal was identified as copper in Fig. 5(f). Therefore, it is inferred that copper played a role in forming spheroidal crystals within abnormal barium titanate grains.

For abnormal grains that contained a number of small BaTiO$_3$ crystals, it is believed that many drops of the liquid phase seemed to be formed and captured due to very fast abnormal grain growth. Some liquid-phase drops greater than the critical size grew or united with one another, creating visible crystal-growth planes. Copper metal was attached to some crystal-growth planes, implying that copper metal may be reprecipitated on the crystal-growth plane during cooling down. But small liquid drops may be dissolved into the abnormal grain so that it becomes smaller than the original particle size. Choi et al. observed captive crystals within abnormal grains during liquid-phase sintering of TaC–TiC–Ni cerments. In their system, Ti would diffuse to the TaC side and reprecipitate as (Ta, Ti)$_2$C. In this case, the driving force for grain coarsening can be given as Eq. (2),

$$\Delta G_{tot} = \Delta G_r + \Delta G_{chem}$$  

where $\Delta G_r$ is the free energy change with coarsening for grain size $a$, and $\Delta G_{chem}$ represents free energy change with formation of solid solution. Such an increased driving force may explain the formation of exceptionally large grains. In this case, the coarsening rate is accelerated when grain boundary re-entrant edges (GBRE), formed by coalescence, are present. Entrapment of small grains into abnormally large grains is believed to be a consequence of the GBRE process.

In the case of Cu$_2$O-added BaTiO$_3$ sintering, the mechanism of entrapped grains is thought to be the same as in the TaC–TiC–Ni system. During liquid-phase sintering of Cu$_2$O-
added BaTiO\textsubscript{3} under N\textsubscript{2} flow, copper diffused into barium titanate and reprecipitated to (Ba, Cu) TiO\textsubscript{3} so that the driving force of grain coarsening due to the chemical composition difference could appear and accelerate abnormal grain growth. The solid solution of Cu\textsubscript{2}O-BaTiO\textsubscript{3} was also confirmed by SEM image, EDX analysis, and EPMA analysis data (Figs. 3, 5, and Fig. 6). A possible explanation is that the GBRE between abnormal grains and small grains accelerated grain coarsening to the extent that small BaTiO\textsubscript{3} grains and the eutectic melt of Cu\textsubscript{2}O-BaTiO\textsubscript{3} were entrapped by abnormal grains; copper was then reprecipitated on the barium titanate crystal-sphere surface and within abnormal grains.

3.3 EPMA

In results of EPMA in Fig. 6, BaTiO\textsubscript{3} crystal spheres, with some copper attached to the surface showed a strong copper peak and weak Ba, Ti, and O peaks. There is another region (B region) in which Ba and O peak intensities were relatively lower than those without crystal spheres, but Ti intensity was almost identical inside and outside the BaTiO\textsubscript{3} crystalline sphere. This means that the crystal sphere has excess Ti over that of the matrix. The BaTiO\textsubscript{3} crystal sphere contained small amounts of copper, even though the matrix had no copper content, as evident in Fig. 6(b). Therefore, we infer that crystal spheres consisted of TiO\textsubscript{2}-excess BaTiO\textsubscript{3} with traces of copper to form the solid solution of (Ba, Cu)TiO\textsubscript{3}. Above the eutectic temperature of 1332°C, abnormal grain growth of TiO\textsubscript{2}-excess BaTiO\textsubscript{3} was thought to result from rapid precipitation of the material through a thin Ti-rich liquid film at grain boundaries. In EPMA of a crystal sphere, it is believed that a crystal sphere could be formed of TiO\textsubscript{2}-excess BaTiO\textsubscript{3} liquid containing copper.

3.4 TEM observations

As is evident in Fig. 7(a), copper grain has slip bands or twins. In electron diffraction pattern analysis results, its zone axis was [011]; the (200) and (111) planes were consistent with its twin planes by rotating 180° along the twin planes (arrow in Fig. 7(b)). A typical grain boundary between BaTiO\textsubscript{3} grains is shown in Fig. 7(c) where the boun-
Microstructural Observations of Cu₂O-Added BaTiO₃ Sintered under N₂ Flow

The faceted grain boundary is faceted with a hill-and-valley structure. Park et al. suggested that abnormal grain growth could occur only when the solid/liquid interface is a singular interface. For grains with a faceted solid/liquid interface, grains can grow only by two-dimensional nucleation or with the assistance of screw dislocations. Lee et al. pointed out that general grain boundaries with high energy should be faceted to have energetically stable configurations. Also, when boundaries are faceted, grains containing twin lamellae can grow quickly because atoms may more easily attach themselves at re-entrant edges than at other faceted boundaries where excess interfacial energy is generated upon atom attachment. Their results demonstrated that when samples of BaTiO₃ were sintered in air below the eutectic temperature, they had abnormally large grains with twin lamellae and faceted grain boundaries. However, after annealing in H₂, faceted grain boundaries became defaceted and all grains grew normally. Grain boundary faceting is necessary for abnormal growth of BaTiO₃ grain. However, in our study, faceted boundaries appeared despite reduced atmospheric pressure ($P_0$ is below $10^{-20}$ atm). Therefore, it is considered that faceted boundaries resulted from the solid/liquid interface between BaTiO₃ and copper, and faceted boundaries hinder normal grain growth to create abnormal grain growth conditions.

4. Conclusions

A BaTiO₃–Cu ferroelectric/metal composite was successfully fabricated by sintering Cu₂O-added BaTiO₃ at a 100 ml/min nitrogen gas flow rates. The copper metal phase was dispersed homogeneously in the matrix; its average size ranged from about 2.4 to 3.4 µm. SEM micrographs revealed that abnormal grain growth occurred at above 1280°C, and that the matrix contained many BaTiO₃ crystal spheres. From EPMA results we inferred that crystal spheres within abnormal grains were formed from excess titanium-contained BaTiO₃ and copper melt, that is, a (Ba, Cu) TiO₃ solid solution. The driving force due to the chemical potential difference arising from the solid-solution accelerated abnormal grain growth, and the grain boundary re-entrant edge (GBRE) mechanism may explain the presence of captive crystals and reprecipitated copper on the surface. TEM micrographs displayed copper metal twins and BaTiO₃ faceted boundaries due to the formation of a solid/liquid interface, which could promote abnormal grain growth.

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