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Microstructural evolution and dielectric properties of SiO_2-doped $CaCu_3Ti_4O_{12}$ ceramics

Kang-Min Kim[a], Sun-Jung Kim[a], Jong-Heun Lee[a,*], Doh-Yeon Kim[b]

[a] Department of Materials Science and Engineering, Korea University, 1,
5-ka, Anam-dong, Sungbuk-ku, Seoul 136-701, South Korea
[b] School of Materials Science and Engineering, Seoul National University,
Seoul 151-744, South Korea

Abstract

The abnormal grain growth (AGG) behavior of undoped and SiO_2-doped $CaCu_3Ti_4O_{12}$ (CCTO) ceramics were investigated. With the addition of 2 wt.% SiO_2, the AGG-triggering temperature decreased from 1100 to 1060 °C, and the temperature for obtaining a uniform and coarse microstructure decreased from 1140 to 1100 °C. The lowering of the AGG temperature by SiO_2 addition was attributed to the formation of a CuO-SiO_2-rich intergranular phase at lower temperature. The apparent dielectric permittivity of coarse SiO_2-doped CCTO ceramics was ∼10 times higher than that of fine SiO_2-doped CCTO ceramics at the frequency of 10^3–10^5 Hz. The doping of SiO_2 to CCTO ceramics provides an efficient route of improving the dielectric properties via grain coarsening. The correlation between the microstructure and apparent permittivity suggests the presence of a barrier layer near the grain boundary.

Keyword: $CaCu_3Ti_4O_{12}$; Grain growth; Grain boundaries; Dielectric properties

1. Introduction

$CaCu_3Ti_4O_{12}$ (CCTO) with the perovskite structure has a large dielectric constant of ∼10,000 to 100,000.[1,2] The large dielectric constant is generally explained by a barrier-layer-capacitor mechanism. However, there are also different suggestions based on the location or formation route of the barrier layer. The high permittivity observed in single crystalline materials has been attributed to the presence of an insulating twin boundary.[3] On the other hand, the microstructure is a key factor in determining the dielectric properties of polycrystalline CCTO ceramics.[4–6] Recently, it was reported that coarse-grained CCTO ceramics (average grain size: ∼>100 μm) sintered at 1100 °C for 20 h shows a permittivity two order of magnitude higher than fine-grained CCTO ceramics (average grain size: ∼5 μm) sintered at 1100 °C for 3 h. They explained the large capacitance in a coarse-grained ceramics in terms of the barrier layer formed at the grain boundary from the complex impedance analysis.[4] Indeed, the presence of a barrier layer at the grain boundary was verified by the observation of nonlinear current–voltage characteristics across a single grain boundary.[6] Therefore, the grain size (frequency of grain boundary) and configuration of the boundary phase such as segregations and/or intergranular phase need to be considered as the key parameters in designing materials with enormous dielectric properties.

The microstructure of CCTO ceramics changes drastically with only a slight variation in the sintering temperature due to the abnormal grain growth (AGG) behavior.[4–6] This again significantly alters the dielectric properties. Accordingly, controlling AGG in CCTO ceramics is of critical importance for obtaining a large and reproducible dielectric constant. The atomically flat interface structure for 2-D nucleation[7,8] and the presence of an intergranular liquid[9–13] for enhanced mass transfer are two important parameters that should be controlled in AGG. Among these, the manipulation of the intergranular liquid is relatively facile.

This paper reports that a SiO_2 impurity promotes AGG in CCTO ceramics. The microstructural evolution of both undoped and SiO_2-doped CCTO ceramics were investigated and compared. Special attention was paid to the role of SiO_2-rich intergranular liquid phase in AGG and its consequent effect on the dielectric properties.

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* Corresponding author. Tel.: +82 2 3290 3282; fax: +82 2 928 3584.
E-mail address: jongheun@korea.ac.kr (J.-H. Lee).

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2. Experimental

High purity $CaCO_3$ (>99%, High Purity Chemical Laboratory Co. Ltd., Sakado, Saitama, Tokyo, Japan), CuO (99.9%, High Purity Chemical Laboratory Co. Ltd., Sakado, Saitama, Tokyo, Japan), and TiO_2 (>99.0%, Aldrich Chemical Co., Milwaukee, WI, USA) were used as the starting materials. The powders were weighed in the appropriate composition (Ca/Cu/Ti = 1/3/4 by molar ratio) and ball-milled for 24 h using a polyethylene jar with ethanol and zirconia balls. The ethanol solvent was removed by rotatory evaporation and the powders were dried at 100 °C for 24 h and pulverized. Single-phase CCTO was obtained by calcining the powders at 1000 °C for 24 h. Although the calcined powder was identified as pure CCTO without any minor phase, the powder was milled again in order to decrease the level of powder agglomeration. The 2 wt.% SiO_2-doped CCTO powder was prepared by ball milling a mixture of CCTO powders and SiO_2 sol (ST-0, solvent water, 20.5 wt.% SiO_2, Nissan Chemical Co., Japan) in an ethanol solvent. The CCTO powder with and without SiO_2 was uniaxially pressed into pellets and then isostatically pressed at 150 MPa. The powder compact was sintered at 1060–1140 °C for 12 h. The sintered pellet was polished using SiC abrasive paper and diamond paste until there was a mirror finish. The electrode was formed by printing a silver paste with subsequent heat-treatment at 600 °C. The apparent dielectric permittivity ($\varepsilon'_{\mathrm{app}}$) and low tangent ($\tan\delta$) of the specimen were measured at frequencies ranging from $1–10^6$ Hz using a dielectric analyzer (Alpha-N, Novocontrol). In order to observe the effect of SiO_2 on the microstructural evolution, a 2 wt.% SiO_2 sol was dropped on the top of the green CCTO compacts using a pipette, dried at 100 °C for 10 h and sintered at 1080 °C for 12 h.

3. Results and discussion

The 2 wt.% of SiO_2 sols were dropped onto the surface of the green CCTO ceramics and sintered at 1080 °C for 12 h. Fig. 1 shows the cross-sectional SEM microstructure of the specimens from the top. The specimen surface consisted of coarse grains sized ∼50 μm. The coarse-grained regime was ∼200 μm thick from the surface. The number of coarse grains decreased towards the center region and finally become a fine microstructure at the center. The very large grains, which were distributed in the matrix of fine grains, indicate the triggering of abnormal grain growth by the addition of SiO_2. Because SiO_2 plays a key role in the microstructural evolution of CCTO ceramics, 2 wt.% SiO_2 was added to the CCTO powder by uniform mixing and the subsequent changes in the microstructures and dielectric properties were investigated.

Fig. 2 shows the microstructural evolution of the undoped CCTO ceramics as a function of the sintering temperature. When sintered at 1080 °C, the microstructure was uniform throughout (Fig. 2(a)) and the grain size ranged from 2 to 5 μm (inset in Fig. 2(a)). At 1100 °C, many coarse grains 10–20 μm in size (circled regions in Fig. 2(b)) appeared in the matrix of fine grains. The coarse grain was significantly larger than the matrix grain, which is indicative of AGG. The microstructure became uniform again as a result of the impingement of abnormally grown grains at 1140 °C (Fig. 2(c)). The specimen consisted of the coarse grains ranging in size from 30 to 50 μm. The results show that AGG behavior is triggered at ∼1100 °C, and a uniform coarse microstructure is attained at ∼1140 °C in undoped CCTO ceramics.

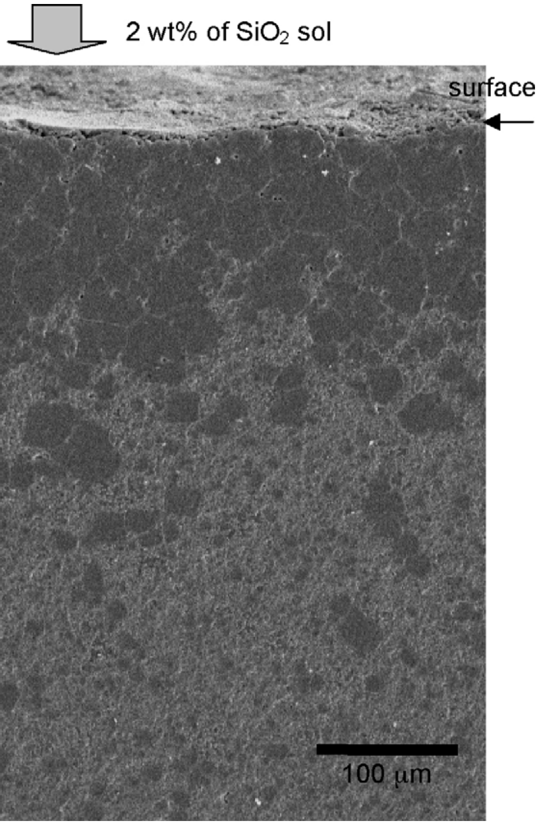

Fig. 1. Cross-sectional microstructure of 2 wt.% SiO_2-dropped CCTO specimen sintered at 1080 °C for 12 h. The 2 wt.% of SiO_2 sol was dropped on the top of a CCTO green compact and sintered.

The microstructural evolution of CCTO ceramics was greatly changed by the addition of SiO_2. When 2 wt.% of SiO_2 was added, a few abnormally grown grains were found even at 1060 °C (circled regions in Fig. 3(a)). The typical size of the abnormally grown grain ranged from 50 to 150 μm. More abnormally grown grains were formed by increasing the sintering temperature to 1080 °C (Fig. 3(b)). Finally, the impingement of abnormally grown grains produced the microstructure coarse and uniform at 1100 °C (Fig. 3(c)). The specimen was composed of coarse grains ranging in size from 50 to 300 μm.

The above results suggest that both the undoped and SiO_2-doped CCTO specimens show AGG and the addition of SiO_2 promotes an AGG behavior. From the literature, the interface structure[7,8] and the presence of a liquid phase[9–11] have been acknowledged as the two main parameters that should be considered in AGG. Spherical grains with an atomically rough interface structure have no energy barrier for atomic attachment during particle growth by Ostwald ripening. Grain growth becomes diffusion controlled, which induces normal grain growth (NGG). However, grains with an angular-morphology have an atomi-

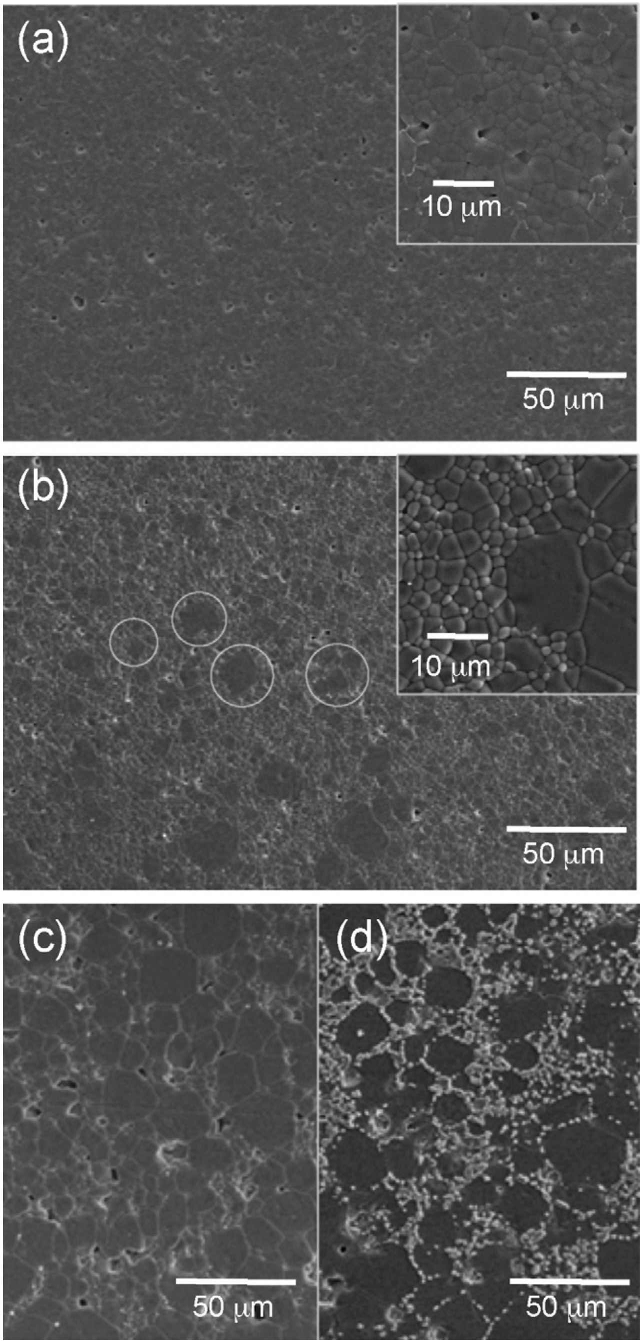

Fig. 2. SEM microstructures of CCTO ceramics sintered at (a) 1080 °C, (b) 1100 °C, and (c), (d) 1140 °C for 12 h.

cally flat (singular) interface structure, which means that there is an appreciable energy barrier for atomic attachment because ledge-generating sources such as 2-D nucleation are required. Due to the significant energy barrier, only a limited number of large grains with sufficient driving force for coarsening can grow rapidly, resulting AGG.

Another key factor in AGG is the presence of an intergranular liquid phase during sintering. The liquid phase can provide an enhanced diffusion path for AGG when the interface structure is atomically flat. Indeed, there are many reports on the promotion of AGG by simply adding a small amount of a liquid phase.[9–13] For example, AGG behavior has been triggered $BaTiO_3$ and $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1}))_3$ by the addition of SiO_2 and CuO, respectively.[12,13]

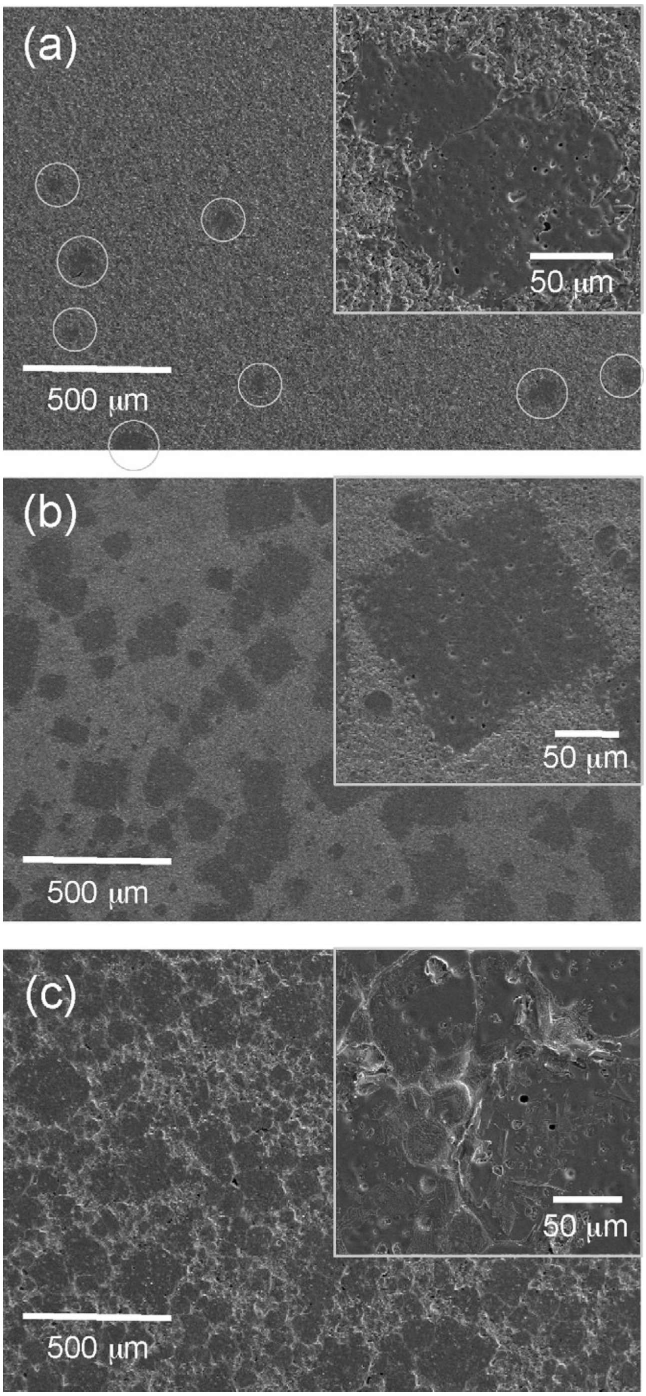

Fig. 3. SEM microstructures of the 2 wt.% SiO_2 doped-CCTO ceramics sintered at (a) 1060 °C, (b) 1080 °C, and (c) 1100 °C for 12 h.

During the microstructural observation, it was found that the surface microstructure of the CCTO ceramics was dependent upon the thermal etching temperature. The microstructure shown in Fig. 2(a–c) was attained by the thermal etching at 1080 °C for 1 h. However, when the thermal etching temperature was lowered to 1020 °C, the intergranular liquid phase was expelled to the outside (Fig. 2(d)). Note that the expelled liquid phase was located on the grain boundary. This intergranular phase was identified as a CuO-rich phase by EDS analysis. Although more study will be needed to determine why the liquid phase is expelled outside as a result of heat-treatment at 1020 °C, a change in the wetting behavior by the oxidation of Cu_2O into CuO < 1025 °C is one possible reason.[14,15] This is consistent with a recent report showing that CuO is segregated at the grain boundary of CCTO ceramics.[5] Abnormally grown grains in the matrix of fine grains showed an angular-morphology (see circled regions in Fig. 2(b)). Accordingly, the AGG behavior of undoped CCTO ceramics results from both of a singular interface structure and the presence of an intergranular liquid phase. The AGG-triggering temperature will be related to the formation temperature of a CuO-rich intergranular liquid phase.

When 2 wt.% of SiO_2 was added to the specimen, the AGG-triggering temperature decreased from 1100 to 1060 °C, and the temperature for obtaining a coarse uniform microstructure decreased from 1140 to 1100 °C. The interface structure of the SiO_2-doped CCTO ceramics can also be regarded as atomically singular from the well-developed angular shape of the abnormally grown grains (Fig. 3(b)). SiO_2 and CuO are one of the most representative sintering agents that decrease the sintering temperature by forming a liquid phase. Accordingly, the addition of SiO_2 can promote AGG by increasing the amount of intergranular liquid. In addition, mixing between SiO_2 and CuO can further lower the liquid forming temperature. According to the CuO-SiO_2 phase diagram,[16] the liquid phase can be formed as low as 1050–1060 °C at a CuO-rich composition when SiO_2 is present. The liquid forming temperature (1050–1060 °C) coincides well with the AGG-triggering temperature of SiO_2-doped CCTO ceramics in this study. Indeed, EDS analysis showed that the Si-component was not at the grain interior but on the intergranular phase. Moreover, XRD showed that both CCTO ceramics with and without SiO_2 doping showed the single CCTO phase (data not shown). This indicates that the SiO_2 component exists in the form of an intergranular liquid phase, which supports the hypothesis that the decrease in the AGG-triggering temperature in SiO_2-doped CCTO ceramics is due to the lowering of a liquid forming temperature and the increase in the amount of liquid.

Fig. 4 shows the dielectric properties of fine and coarse SiO_2-doped CCTO ceramics and the coarse undoped CCTO ceramics. The fine SiO_2-doped CCTO ceramics (sintered at 1060 °C) showed an apparent relative permittivity (ε'_{app}) of 3,300–3,600 at 10^3–10^5 Hz and minimum $\tan\delta$ of 0.0346 at 36.5 kHz. In contrast, coarse SiO_2-doped ceramics (sintered at 1100 °C) showed ε'_{app} of 26,000–32,600 at 10^3–10^5 Hz and minimum $\tan\delta$ of 0.114 at 15.4 kHz. The approximately ~10 fold increase in ε'_{app} by grain coarsening indicates that the barrier layer mechanism plays a role in the enormous dielectric properties. The ε'_{app} value of the coarse pure CCTO specimen was approximately 2–2.5 times higher than that of the coarse SiO_2-doped CCTO ceramics. The decrease in ε'_{app} by SiO_2 doping can be explained by a thickening of the intergranular liquid phase. However, the frequency for minimum $\tan\delta$ increased from ~0.1 to ~25 kHz and minimum $\tan\delta$ value did not deteriorate significantly when doped with SiO_2. This suggests that the frequency at the minimum loss tangent can be shifted to a higher frequency regime by adding SiO_2 without any significant decrease in ε'_{app}.

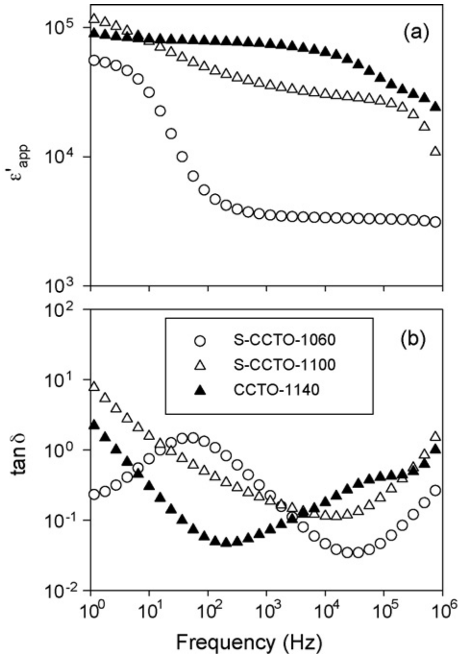

Fig. 4. (a) Apparent relative permittivity (ε'_{app}) (b) loss tangent ($\tan\delta$) of pure and 2 wt.% SiO_2 doped-CCTO specimens: S-CCTO-1100 (2 wt.% SiO_2 doped, sintered at 1100 °C for 12 h); S-CCTO-1060 (2 wt.% SiO_2 doped, sintered at 1060 °C for 12 h); CCTO-1140 (pure, sintered at 1140 °C for 12 h).

In summary, the coarsened microstructure of CCTO ceramics, which is advantageous for the dielectric properties can be attained at a lower sintering temperature by adding SiO_2. The microstructure, ε'_{app} and the frequency at minimum $\tan\delta$ was dependent on SiO_2 doping. SiO_2 is the most ubiquitous impurity and can be included during ceramic processing and sintering procedure. Therefore, complete removal of SiO_2 impurity is very difficult. These results suggest that the SiO_2 impurity should be controlled tightly in order to achieve a reproducible microstructure and dielectric properties.

4. Conclusions

The addition of SiO_2 to $CaCu_3Ti_4O_{12}$ (CCTO) ceramics lowered the temperature for abnormal grain growth significantly. In pure CCTO ceramics, AGG was triggered at 1100 °C, and the microstructure becomes homogeneous and coarse at 1140 °C as a result of the impingement of abnormally grown grains with each other. In contrast, 2 wt.% of SiO_2 doping decreased the temperature for triggering AGG to 1060 °C and decreased the temperature for obtaining a coarse and uniform microstructure to 1100 °C. The lowering of the AGG temperature with the addition of SiO_2 was explained by the formation of a more CuO-SiO_2-rich intergranular liquid at the lower sintering temperature. When 2 wt.% SiO_2 was added to CCTO, the coarse-microstructured specimen showed a ~10 times higher apparent dielectric permittivity than the fine-microstructured one at a frequency of 10^3–10^5 Hz, which supports the barrier-layer-capacitance model at the grain boundary.

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