

Decomposition Reactions in CaCu₃Ti₄O₁₂ Ceramics

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 $CaCu_3Ti_4O_{12}$ (CCTO) ceramics sintered in air at 1115°C for 3 and 24 h have been heat treated in N₂ at 1000°C. Surface layers develop on the outer regions of the ceramics, and a combination of X-ray diffraction and analytical electron microscopy has been used to establish the phase content of the layers. A model to explain the formation of the surface layers is proposed based on decomposition of CCTO into a mixture of CaTiO₃, TiO₂, and Cu₂O. The role of limited decomposition in the development of electrically inhomogeneous CCTO ceramics prepared at elevated temperatures in air is discussed.

I. Introduction

HERE is currently considerable interest in an unusual perovskite-related oxide CaCu₃Ti₄O₁₂ (CCTO)¹⁻³ as a potential material for internal barrier layer capacitor (IBLC) applications. It is now generally accepted that CCTO ceramics prepared in air at $>1000^{\circ}$ C are electrically heterogeneous, consisting of *n*-type semiconducting grains and insulating grain boundaries,³⁻⁵ thereby possessing the required electrical microstructure of an IBLC. The advantage of CCTO compared with other titanate perovskites such as (Ba,Sr)TiO3-based ceramics (BST) for IBLC applications is that the electrical microstructure can be developed in a single processing step in air and therefore avoid the multi-step processing routes required for BST. The defect chemistry and microstructural development associated with the multi-step processing route of BST ceramics is now reasonably well understood and has been developed over many years to optimize the IBLC characteristics of these materials. In contrast, the defect chemistry and evolution of ceramic microstructure of CCTO remain poorly understood. Establishing the origin of the *n*-type semiconductivity in CCTO and the composition of the grain boundary regions in CCTO ceramics remain challenging and important problems, especially if these materials are to be optimized for IBLC or related applications in the near future.

Two models have been proposed for the *n*-type semiconductivity in CCTO. The first involves oxygen loss, viz., CaCu₃Ti₄O_{12- δ}, as is commonly observed for many titanatebased perovskites such as BST⁶ when heated at high temperatures and/or under reducing atmospheres. Although the level of oxygen loss is often small, $\delta \ll 0.01$, it is sufficient to change electrically insulating Ti-based perovskites such as BST from an off-white/cream color with a bulk resistivity in excess of 10^{10} $\Omega \cdot$ cm at room temperature (RT), into a dark-blue color with an RT bulk resistivity $\sim 0.1-10 \ \Omega \cdot$ cm. The blue color and *n*-type semiconductivity are due to partial reduction of Ti⁴⁺ (*d*^o) to Ti³⁺ (*d*¹) associated with the oxygen loss from the lattice.

The second model has been proposed recently by Li *et al.*⁷ and is based on the thermodynamic fact that CuO is unstable in air above $> 1065^{\circ}$ C and reduction to Cu₂O should occur. CCTO

ceramics are commonly sintered in the range $\sim 1000^{\circ}$ -1100°C, and therefore, in this model, reduction of $\check{C}u^{2+}$ to Cu^+ occurs at these high temperatures with charge compensation by partial occupation of the Cu site by Ti⁴⁺ according to the formula $Ca(Cu_{1-3x}^{2+}Cu_{2x}^{+}Ti_{x}^{4+})_{3}Ti_{4}O_{12}$. On cooling to RT, the monovalent Cu⁺ ions are re-oxidized to Cu²⁺ ions and an internal redox process occurs, causing partial reduction of Ti⁴⁺ to Ti³⁺ ions on the B-site sublattice leading to the formula $Ca(Cu_{1-x}^{2+}Ti_x^{4+})_3Ti_{4-6x}^{4+}Ti_{6x}^{3+}O_{12}$, and *n*-type semiconductivity. As has been pointed out by Li *et al.*,⁷ only small levels of either oxygen non-stoichiometry (model 1) or cation non-stoichiometry (model 2), x < 0.001, are required to induce the level of RT bulk semiconductivity (~10-100 $\Omega \cdot cm$) commonly observed for CCTO ceramics. It is therefore likely to be very difficult to distinguish between these two models by direct chemical analysis; however, some form of Cu-rich secondary phase(s) should be detected for model 2 in samples prepared from a starting composition of stoichiometric CaCu₃Ti₄O₁₂, assuming negligible volatility of Cu at high temperatures.

Recently, we have reported electron probe microanalysis (EPMA) on CCTO ceramics sintered for 24 h in air at 1115°C.8 The results revealed the presence of Cu₂O within the ceramics and more significantly, the CCTO grains to be Cu deficient with an average composition Ca_{0.98(2)}Cu_{2.92(2)}Ti_{4.04(2)}O₁₂ (only cation contents were determined). In addition, dramatic changes in phase assemblage were observed for CCTO ceramics heat treated in N₂ at $>800^{\circ}$ C with the development of surface layers. Impedance spectroscopy was used to showed that the RT bulk resistivity of $\sim 100 \ \Omega \cdot$ cm observed in CCTO ceramics sintered in air was insensitive to heat treatment in N₂ or O₂ at 800°-1000°C.9 In contrast, the RT grain boundary resistance showed substantial variation with post-heat treatment, decreasing by three to four orders of magnitude after heat treatment in N2. The resistance of the grain boundaries could be recovered to values close to the air-sintered values when heat treated in O₂ at 1000°C. These results have led us to suggest that origin of the semiconductivity in CCTO is more probably related to cation non-stoichiometry (model 2) than to oxygen loss (model 1).

To the best of our knowledge, the thermal stability of CCTO ceramics under various heat-treatment conditions (temperature and oxygen partial pressure) has not been established. Here, we report phase analysis by X-ray diffraction (XRD), thermal analysis, and analytical electron microscopy results on CCTO ceramics that have been sintered in air at 1115°C and then heat treated in an inert (flowing N₂) or reducing (flowing 5% H₂/95% Ar) atmosphere at 1000°C. Characterization of the surface layers that develop on CCTO ceramics under the inert conditions provides further insights into the important role of the instability of Cu²⁺ in CCTO ceramics sintered in air at high temperatures.

II. Experimental Procedure

High-purity CaCO₃, CuO, and TiO₂ reagents (all 99.99% pure, Aldrich Chemical Co., Milwaukee, WI) at a molar ratio of 1:3:4 were mixed in a planetary ball mill (Fritsch GMBH model pulverisette 6, Albishein, Germany) with acetone using an agate pot and balls (a mixture of 5 and 10 mm balls) at 250 rpm for 20 min. After drying, the powder (~10 g) was reacted in air over-

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night at 1000° C on a Pt foil and then milled again at 250 rpm for 30 min before a second reaction at 1000° C. The powder was then planetary ball milled at 250 rpm for 60 min.

XRD was performed on powder samples using a high-resolution diffractometer (Stoe StadiP, Stoe and Cie GmbH, Darmstadt, Germany) operated at 50 kV and 30 mA (step size of scan 0.02° and scan rate 2°/min) to assess phase purity. XRD on pellet surfaces was performed using a Siemens (Karlsruhe, Germany) X-ray diffractometer with CuK α_1 radiation. Particle size analysis (Model Coulter LS 130, Beckmann, High Wycombe, UK) showed a bimodal particle size distribution in the powder at ~0.4 and 6 µm and a d_{50} value of ~3.4 µm.

 $CaCu_3Ti_4O_{12}$ powder compacts were pressed in a 10 mm steel die at 0.5 ton and sintered at 1115°C in air for either 3 or 24 h, and furnace cooled to RT. Pellet densities were calculated from the mass and dimensions of the pellets and all were >95% of the theoretical density.

Ceramics for scanning electron microscopy (SEM) were prepared by mounting in resin and polishing sections perpendicular to the major pellet faces. The polished ceramics were carbon coated and analyzed using a JEOL JSM-6400 SEM (Jeol Ltd., Tokyo, Japan) equipped with a LINK energy-dispersive X-ray (EDS) detector and ancillary electronics operating at 20 kV. The as-sintered surface of 24 h ceramics was analyzed by XRD, and then polished with SiC paper and re-measured; the process was repeated until the sample was ~80% of the original thickness. The ceramic microstructures of pellets sintered for 3 and 24 h consist of average grain sizes of ~5 and >100 μ m, respectively. Details of the ceramic microstructures have been reported previously.⁴

Hydrogen-reduction thermogravimetry (TG) in 5% $H_2/95\%$ Ar (heating rate 10°C/min, reference Al₂O₃) was performed on powder (~50 mg) from a crushed 24 h pellet.

As-sintered 3 and 24 h ceramics were placed on a Pt foil, inserted into a tube furnace, and heat treated in oxygen-free N₂ for 6 h at 1000°C (heating rate 5°C/min, cooling rate 2.5°C/min). A 3 h heat-treated ceramic was analyzed by XRD as a function of pellet thickness as described above. Finally, samples of 3 and 24 h heat-treated ceramics were prepared for SEM as described above.

III. Results and Discussion

Low- and high-magnification backscattered electron images (BEI) of as-sintered 3 and 24 h ceramics, viewed as a cross section perpendicular to the major pellet faces, are shown in Fig. 1. At low magnification, the 3 h sample appears homogeneous without large-scale flaws, such as fissures, or pores over 5 µm in diameter, Fig. 1(a), whereas the 24 h sample reveals a coarser pore structure with pore sizes up to 30 µm, Fig. 1(b). At higher magnification a fine-grained texture ($<10 \mu m$ in size) is evident for the 3 h sample, and the pore structure, observed as black voids, is closed. A secondary phase was observed as bright precipitates in a number of pores and, in particular, at grain boundary junctions, Fig. 1(c). The grain structure of the 24 h sample was much coarser, although it was not possible to assess accurately as the samples were not etched, but previous results have shown that the grains are typically between 100 and 300 µm in size.⁴ A secondary phase was detected as bright precipitates using BEI, Fig. 1(d), consistent with that observed for the 3 h ceramic. An additional secondary phase for the 24 h sample was observed in BEI as dark spherical precipitates of $\sim 5 \,\mu m$ diameter, Fig. 1(d).

A typical EDS spectrum of the main CCTO phase in both 3 and 24 h samples is shown in Fig. 2. The observed peaks correspond to known peak positions for Ca, Cu, and Ti. Although the EDS data do not provide a direct means to quantify the composition of a particular region, the data are representative of the bulk CaCu₃Ti₄O₁₂ phase, consistent with analysis performed by EPMA and reported previously.⁸ Figure 2(b) shows typical EDS data for the bright phase observed at the grain boundary junctions in the samples. The two major peaks correspond to known peak positions for Cu and are commensurate with the



Fig. 1. Backscattered electron images scanning electron microscopy showing cross sections of (a) 3 h and (b) 24 h $CaCu_3Ti_4O_{12}$ ceramics at low magnification and high magnification (c and d, respectively).



Fig. 2. Typical energy-dispersive X-ray spectra of (a) bulk $CaCu_3$. Ti_4O_{12} phase and secondary phases observed by backscattered electron images as (b) bright precipitates and (c) dark spherical precipitates.

Cu₂O phase, also detected by EPMA.⁸ The secondary peaks correspond to Si, Ca, and Ti, which may arise from the precipitate itself, or from surrounding material if the interaction volume exceeds the volume of the precipitate during the EDS analysis. The EDS data in Fig. 2(c) are typical of the dark phase observed in the 24 h sample, with major peaks corresponding to Si, Ca, and Ti, and a minor peak corresponding to Cu. The morphology and composition (according to the EDS data) are consistent with CaTiSiO₅ (sphene) precipitates observed by EPMA, as reported previously.⁸ The Cu signal may arise from incorporation of Cu into the sphene lattice or as a result of interaction of the primary beam with the surrounding area. The presence of Si arises due to unintentional contamination from the milling media used in the powder processing.

Representative XRD data for as-sintered and polished surfaces of CCTO ceramics prepared in air at 1115°C are shown in Fig. 3. All reflections from the as-sintered pellet surface with the exception of a small peak at ~36.5° correspond to the pattern reported in the literature¹⁰ and ICDD card number 75-2188 for CaCu₃Ti₄O₁₂. The additional minor peak observed at ~36.5° in the as-sintered pellet surface (see the inset in Fig. 3) was removed on polishing the pellet surface as the most intense peak in the XRD pattern for Cu₂O (ICDD card number 77-199) is the (111) reflection at 36.521°. Unfortunately, the second most intense peak (200 reflection) for Cu₂O occurs at 42.423°, which is close to the (111) reflection for CCTO; see the inset in Fig. 3. All remaining peaks for Cu₂O have relative intensity <30%, and given the small volume fraction of the impurity phase, which was limited only to the as-sintered pellet surface,



Fig. 3. Typical X-ray diffraction patterns obtained from an as-sintered pellet surface (bottom trace) and then, sequentially, from layer-by-layer polished pellet surfaces (upper traces).

it is not possible to attribute unequivocally the extra reflection to Cu_2O .

Low-magnification BEI images of 3 and 24 h samples heat treated in N_2 for 6 h at 1000°C are shown in Fig. 4. The image contrast reveals two compositionally distinct layers surrounding the bulk CaCu₃Ti₄O₁₂ material in both samples; these layers appear to form a "decomposition zone," Fig. 4(a) and (b). A higher magnification image for a 3 h sample shows the interface between the outer two layers, Fig. 4(c) (a similar image, not shown, was obtained for a 24 h sample) and the interface between the inner layer and bulk material, Figs. 4(d) and (e). The outermost layer was a highly porous ($\sim 50\%$ dense), "corallike" structure of $\sim 1 \,\mu m$ diameter interconnected strands. This structure forms the matrix of an inner layer in which the pores are filled with a phase that appears brighter than the matrix. In both samples, the thickness of the layers varies greatly such that, for 3 h samples, the outer layer can extend $\sim 100 \ \mu m$ into the sample or, conversely, the inner layer can extend from the bulk interface, through the outer layer and to the pellet surface. The overall thickness of the decomposition zone was relatively constant in both samples. For the 3 h sample, the decomposition zone thickness was $\sim 150 \ \mu m$ at the major pellet faces, increasing to $\sim 200-300 \ \mu m$ along the pellet circumference. The decomposition zone was thinner in the 24 h sample, ~100-150 µm.

Typical EDS data for the bright precipitate phase and matrix phase observed in the decomposition zone are shown in Figs. 5(a) and (b), respectively. The bright phase corresponds to a copper-rich phase, which is confirmed by XRD (see later) to be Cu_2O . The presence of Ca and Ti in the EDS data may, as before, arise from their incorporation into the Cu_2O lattice and/or from beam interactions with surrounding material. The dark matrix contains Ca, Ti, and Si, and XRD (see later) is used to show evidence of several phases, including CaTiO₃ and TiO₂.

For both samples, the interface between the inner layer and the bulk material, Figs. 4(d)–(e), is clearly defined by a fine texture of Cu₂O striations originating from the CaCu₃Ti₄O₁₂ grains and, below the interface, the microstructure is comparable both in terms of grain size, porosity, and distribution of secondary phase(s) to that of the as-sintered samples in Fig. 1. The texture is clearly less striated in the 3 h sample, such that the striations extend for 5–10 μ m before coalescing into a more "globular" morphology, Fig. 4(d). The inner layer of the 24 h sample, however, was entirely striated between the interface with the outer layer and the interface with the bulk material, Fig. 4(e).

The crystalline phases contained within the decomposition zone and the bulk material for samples heat treated in N_2 at 1000°C were characterized by XRD; layer-by-layer and typical



Fig. 4. Low-magnification backscattered electron images scanning electron microscopy (BEI SEM) of (a) 3 h and (b) 24 h samples in cross section after heat treatment at 1000°C in N₂. BEI SEM showing interface between the outer layer and the inner layer of the decomposition zone in (c) 3 h sample after heat treatment at 1000°C in N₂. BEI SEM showing interface between the bulk phase and the inner layer of the decomposition zone of (d) 3 h and (e) 24 h samples.

results are shown in Fig. 6. As-sintered $CaCu_3Ti_4O_{12}$ pellets were black in color, whereas those heat treated at 1000°C in N₂ were white. Light polishing of the pellet surfaces of the heattreated samples resulted in a sequence of color changes from white to orange, then dark brown, and finally black. These changes are macroscopic evidence for the existence of the two layers in the decomposition zone and the bulk material below, as observed by SEM. XRD data were obtained from the various colored pellet surfaces, as summarized in Fig. 6. The bottom trace in Fig. 6 shows the XRD data for the original white surface, and subsequent data sets are for the orange surface (layer 1), dark brown surface (layer 2), and finally the black surface (layer 3 and bulk).

Reflections observed from the white surface correspond to TiO_2 (rutile), (ICDD card 21-1276) and $CaTiO_3$ (ICDD card 22-153), in agreement with EDS data obtained from the outer layer and inner layer matrix. There is no evidence of $CaCu_3Ti_4O_{12}$ or any crystalline Cu-containing oxides. In addition, there was no evidence for sphene or crystalline SiO₂ in the XRD data, suggesting that the Si detected by EDS was either present in an

amorphous silicate phase or incorporated into the TiO₂ and/or CaTiO₃ lattice, or in such small quantities that it could not be detected by laboratory XRD. The change in pellet surface color from white to orange coincides with the observation of extra reflections corresponding to Cu₂O (Fig. 6, layer 1). This is most clearly observed by the appearance of the (311) reflection at ${\sim}73.7^{\circ}$ for Cu₂O; unfortunately, the most intense peak for Cu₂O, at ~36.5°, the (111) reflection, occurs in the vicinity of the second most intense peak, (101) reflection, for rutile. This confirms the major precipitate phase of the inner layer to be Cu_2O , and the outer layer "coral" structure of TiO_2 and $CaTiO_3$ also forms the matrix of the inner layer. Further polishing, until the change in color from orange to dark brown, yielded reflections in the XRD pattern corresponding to CaCu₃Ti₄O₁₂, Cu₂O, TiO₂, and CaTiO₃ (Fig. 6, layer 2). After further polishing, all reflections were found to correspond to CaCu₃Ti₄O₁₂ (Fig. 6, layer 3 and bulk).

Hydrogen reduction TG was performed on a small amount of powder from a crushed pellet sintered in air at 1115° C for 24 h. Weight loss commenced at ~330°C and was complete by



Fig. 5. Typical energy-dispersive X-ray spectra from (a) the bright precipitate phase in the inner layer of the decomposition zone and (b) the matrix phase in the inner and outer layer.

~680°C, with a total mass loss of ~8%. XRD of the remaining powder following the TG experiment revealed no trace of the original CCTO phase. Instead, the sample consisted of CaTiO₃, TiO₂ (Rutile), and metallic Cu, Fig. 7, indicating complete decomposition of CCTO. The observed mass loss of ~8% is in good agreement with that expected for the reduction of Cu²⁺ to Cu metal (7.8% mass loss) for an initial starting composition of CaCu₃Ti₄O₁₂. Although it is clear that CCTO ceramics are inhomogeneous, the overall decomposition process in reducing conditions can be described by the following equation:

$$\begin{array}{l} CaCu_{3}Ti_{4}O_{12} \rightarrow CaTiO_{3} + 3 TiO_{2} + 3 Cu \\ + 3/2 O_{2} \left(g\right) \end{array} \tag{1}$$

The decomposition process occurring in CCTO ceramics at 1000° C in N₂ is incomplete, presumably because of kinetic effects associated with the limited heat-treatment time of dense ceramics for 6 h in an inert atmosphere as opposed to a small amount of crushed powder in a reducing atmosphere. Nevertheless, the results for the N₂ heat-treated CCTO ceramics can



Fig. 6. X-ray diffraction data of the ceramic surface for a 3 h sample after heat treatment at 1000° C in N₂ (bottom trace) and then, sequentially, from layer-by-layer polished pellet surfaces (upper traces).



Fig. 7. X-ray diffraction pattern of phase assemblage following TGA of CaCu₃Ti₄O₁₂ powder heated to 1100° C in a 5% H₂ atmosphere.



Fig.8. Schematic illustration of decomposition reactions occurring in $CaCu_3Ti_4O_{12}$ ceramics heat treated at 1000°C in N_2 .

be summarized schematically in Fig. 8. At the interface of the bulk phase and the decomposition zone, CaCu₃Ti₄O₁₂ decomposes into a phase mixture of CaTiO₃, Cu₂O, and TiO₂ (this discussion is simplified to exclude oxygen loss from the bulk phase and/or secondary phases and the presence of SiO₂ contamination). The inner layer contains the reaction products, in which CaTiO₃ and TiO₂ coexist as a matrix structure and Cu₂O as a precipitate within that matrix. At the interface between the outer and inner layers of the decomposition, volatilization of Cu₂O occurs, leaving the CaTiO₃-TiO₂ matrix to form a porous, "coral-like" outer layer. As stated previously, the electrical properties of the polished CCTO ceramics after removal of the surface layers showed the bulk resistivity to be unaltered by the heat treatment in N2 at 1000°C; however, the grain boundary resistivity decreased by three to four orders of magnitude.⁹ This result indicates that the composition of the grain boundary regions in CCTO changes significantly during heat treatment and presumably, decomposition commences along the grain boundaries in CCTO ceramics where mass diffusion of primarily Cu and O is significantly higher than that occurring within the grains. The lack of variation in bulk resistivity for samples heat treated in N₂ or O₂ suggests that the oxygen-loss model (model 2) is unlikely to be the primary source of semiconductivity in CCTO ceramics.

Such large-scale decomposition was not observed in as-sintered samples, although isolated precipitates of Cu₂O and CaTiSiO₅ were observed in samples sintered in air at 1115°C for 24 h. In addition, XRD of pellet surfaces indicate the possible presence of Cu₂O, and other workers have reported the presence of "Cu-rich" grain boundaries in CCTO ceramics sintered at elevated temperatures.¹¹

IV. Conclusions

The results presented here suggest that limited reduction and decomposition processes may play a central role in the development of the electrical microstructures observed for CCTO ceramics sintered in air at $>1050^{\circ}$ C. Further investigations using analytical transmission electron microscopy are in progress to probe nanoscale compositional variations in the grain and

grain boundary regions of CCTO ceramics. This should provide more information regarding the composition–electrical property relationships in CCTO ceramics.

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