Local Structure Analysis of Cubic Perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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Recently, there has been considerable interest in the dielectric properties of the cubic perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The material has shown to have relatively high temperature independent dielectric permittivity over a wide temperature range from 100 K to 600 K. Below ~ 100 K the permittivity drops by almost three orders of magnitude, but is not accompanied by a structural phase transition. We studied $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ hoping to find signatures of local structural distortions that may explain the observe anomalies in the dielectric properties. Experiments were carried out using synchrotron radiation at several temperatures between room temperature and 10 K. Reconsideration is necessary for interpreting a huge permittivity by the local disorder model.

Key words: pair-distribution function, synchrotron X-ray diffraction, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

1. INTRODUCTION

Recently, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) was discovered to possess one of the largest static dielectric constants ever measured, reaching nearly $\epsilon_0 \sim 80000$ for single-crystal samples at room temperature [1-3]. Remarkably, the enormous static susceptibility is almost constant over a wide temperature range ($\sim 0 - 500$ K). Moreover, measurements of the dynamic susceptibility show that ϵ falls from its huge static value to a more conventional $\epsilon \sim 100$ with increasing frequency, and that this crossover shows a Debye-like frequency dependence (e.g., $\tau^{-1} \approx 1$ kHz at 80 K) with a relaxation rate τ^{-1} exhibiting an activated dependence on temperature. However, the physical origins of the enormous ϵ_0 and the related Debye relaxation process remain mysterious.

At present, it is difficult to explain the origin of the huge dielectric constant as intrinsic phenomena. In view of the experimental and theoretical difficulties, it has come to be thought that the large observed static dielectric response arises from extrinsic mechanisms, such as point, line, or planer defects, or more generally, with sample microstructure, morphology, or boundary layers. If such boundaries or interfaces exist, they could possibly give rise to a large dielectric response by so-called Maxwell-Wagner effect. The aspect of this model is that they require the insulating blocking layers to be so uniform and robust that they completely prevent conductivity of the samples as a whole, despite their small volume fraction. In fact there are hints of such behavior in the experimental work [4]. The dielectric constant of CCTO shows clear grain size dependence.

The crystal structure of CCTO is body-centered cubic with four ATiO_3 perovskite-type formula units per

primitive cell (where A is either Ca or Cu). The doubled conventional 40-atom unit-cell is shown in Fig. 1. The local moments associated with d holes on the Cu^{2+} cations result in the formation of long-range magnetic order; transport, Raman, and neutron diffraction experiments indicate that CCTO is an antiferromagnetic insulator having a Néel temperature T_N of 25 K [1,2,5]. Thus, the 40-atom simple-cubic cell in Fig. 1 is also the primitive cell of the spin structure. Although the extraordinary dielectric behavior persists far above the temperature scale of the magnetic order, the influence of the strongly correlated local moments, which will likely

Fig. 1. Structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), showing TiO_6 tilting octahedra. While large, middle, and small atoms are Ca, Cu, and O, respectively. Solid lines indicate 40-atom primitive cell of antiferromagnetic spin structure.

remain above T_N , is currently unknown.

In this paper, we studied $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ hoping to find signatures of local structural distortions that may explain the observed anomalies in the dielectric properties. Local structure analysis was carried out using synchrotron X-ray pair-distribution function (PDF) method. The PDF technique has long been used to characterize structures of glasses, liquids, and amorphous materials and recently found its application to study local structures of disordered crystalline materials. The PDF measures the probability of finding an atom at a distance r from another atom. One of the advantages of the PDF method over other local probes such as X-ray absorption fine structure (XAFS) is that it gives both local and intermediate range information, because both Bragg peaks and diffuse scattering are used in this analysis. The PDF analysis can reveal the deviation from the average structure.

2. EXPERIMENTAL

All samples were in a polycrystalline form and were prepared by a solid-state reaction. Dried starting materials of CaCO_3 , CuO , and TiO_2 were mixed and baked at 800°C . Then, the mixtures were ground and fired again at $1040^\circ\text{C} \sim 1100^\circ\text{C}$ to make the single-phase powder of CCTO.

The magnetic measurements were carried out with a superconducting quantum interface device (SQUID) magnetometer. Optical microscopy of the sample surface, as well as scanning electron microscopy (SEM), using a JEOL-JSM-5400 scanning microscope, were utilized to check the surface morphology before X-ray measurements. The dielectric measurements were performed with an LCR meter (HP-4284A).

Synchrotron X-ray powder diffraction data were collected at room temperature with 60 keV X-rays at BL14B1 of SPring-8, which is a bending magnet beamline. The incident beam was focused 3 mm by sagittal focus bender [7]. Conventional powder diffraction was performed to collect crystalline CCTO with transmission geometry.

3. RESULTS

3.1 Grain size vs dielectric constant

The grain size of CCTO was controlled by sintering temperature. The grain size increased as the sintering temperature increased. The larger the grain size was, the higher the dielectric constant of CCTO was. We performed the structure analysis for two CCTO samples those were sintered at 1040°C and 1100°C . The grain size and dielectric constant of these samples are shown in Table. I. It is noted that, the magnetic transition temperature was almost same in these two samples.

Table. I Grain size and dielectric constant for CCTO samples

Sintering Temp. ($^\circ\text{C}$)	Grain size (nm)	ϵ
1040	3	2810
1100	30	53700

Fig. 2. Powder X-ray diffraction pattern for 1040°C -sintered CCTO ($R_{\text{WP}} \sim 13.42\%$) fitted with the space group $Im\bar{3}$. The cross markers and upper solid lines stand for the experimental and calculated patterns, respectively. The lower solid lines show the difference between the experimental and calculated patterns. The vertical markers are the calculated Bragg angles. The large 2θ region is expanded in the inset.

3.2 Average structure

Figure 2 shows the X-ray diffraction pattern of CCTO sintered at 1040°C . The experimental patterns could be fitted with cubic $Im\bar{3}$ structure. The lattice parameter of the 1040°C -sintered sample is $a = 7.3287(9)$ Å, which is very close to that reported previously. The fitting result of the 1100°C -sintered CCTO was also agreed. However, the lattice parameter of the 1100°C -sintered CCTO was a little shorter than that of the 1040°C -sintered CCTO, as shown in Fig. 3. In general, an increase of lattice parameter in the perovskite oxides means the existence of oxygen deficiency. The more oxygen deficiency should exist in the 1040°C -sintered CCTO, but the difference is very small, estimating from the shift of Bragg peaks.

Fig. 3. X-ray diffraction patterns of 1100°C -sintered and 1040°C -sintered CCTO. The peak positions of 1040°C -sintered CCTO shifted to higher angle, indicating the elongation of lattice constant.

Fig. 4. (a) Reduced structure function of CCTO. (b) Corresponding PDFs of CCTO. Dashed and solid lines show 1100°C- and 1040°C-sintered CCTO.

3.3 PDF analysis

The sample dependent single scattering, $S(Q)$, was obtained using standard procedures [8,9]. The data were corrected for absorption, multiple scattering, and polarization effects. Background and Compton scattering were removed and the data were normalized for flux and number of scatterers. In this work, the upper limit of $Q_{\max} = 25 \text{ Å}^{-1}$ was used. This is necessary to obtain a high-resolution PDF. The reduced structure factor $F(Q) = Q[S(Q) - 1]$ for 1040°C-sintered and 1100°C-sintered CCTO are shown in Fig. 4 (a). The fact that the Bragg peak intensity appears at high- Q region in both samples reflects that there are rigid long-range order structures without significant atomic scale disorder in these compounds.

The experimental PDF, $G(r)$, is obtained by taking the Fourier transform of the reduced structure factor $S(Q)$, according to the following equation:

$$G(r) = \frac{2}{r} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ \quad (1).$$

The resulting PDFs are shown in Fig. 4 (b). The obtained PDFs of 1100°C- and 1040°C-sintered CCTO were very similar. The middle-range order structure of these samples are almost same, as well as the average structure. However, the PDF amplitude of the 1040°C-sintered CCTO is larger than that of 1100°C-sintered CCTO, indicating that mosaic block size of the 1040°C-sintered CCTO is larger than that of the 1100°C-sintered CCTO.

Fig. 5. Temperature evolution of local structure of 1040°C-sintered CCTO from 300 K to 10 K.

Figure 5 shows PDF spectra of the 1040°C-sintered CCTO from 300 K to 10 K in the r range $1 < r < 10 \text{ Å}$. Here we notice that significant change was not observed in this temperature range. The dielectric constant increases remarkably around 100 K. However, local structure did not fluctuate at 100 K. A structural disorder to cause a huge dielectric permittivity does not exist.

We tried to reproduce the experimental PDF by the

Fig. 6. (a) Model PDF of the 1100°C-sintered CCTO using results of the Rietveld refinement (solid line) compared with the experimental data (circles). (b) Model PDF of the 1040°C-sintered CCTO using results of the Rietveld refinement (solid line) compared with the experimental data (circles).

average structure. Figures 6 (a) and (b) show the comparison between the observed PDF and calculated PDF using the parameters obtained by the Rietveld refinement in the 1100°C- and 1040°C-sintered CCTO, respectively. The agreement is clearly very good, indicating that the difference between the local and average structures is very small. However, the local structure of the 1100°C-sintered CCTO is somewhat different from that of the 1040°C-sintered CCTO. The comparison of the local structures of these samples is shown in Fig. 7. A remarkable difference is found in the nearest-neighbor and second nearest-neighbor PDF peaks, indicated by arrows in Fig. 7. In the CCTO crystal structure, the nearest-neighbor bond distance is Ti-O, as shown in Fig. 1. One of a possible reason of the peak broadening is oxygen deficiency. If the oxygen deficiency exists, the chemical ordering of A-site atoms (Ca/Cu) may be fluctuated. As a result, the anti-phase domain boundary was formed. Therefore, the amount of the oxygen deficiency does not change so between the two samples, the difference in the local structure was not small.

4. DISCUSSION

The PDF analysis revealed that the coherency of the local structure of the 1100°C-sintered CCTO improved compare to that of the 1040°C-sintered CCTO. On the other hand, the mosaic block size of the 1100°C-sintered CCTO was smaller than that of the 1040°C-sintered CCTO. In ferroelectric materials, the mosaic block size is reduced by the formation of ferroelectric domain. It is necessary to assume the domain structure to explain the increase of the mosaic block size. However, we could not find the evidence of the ferroelectric feature in the average structure. There are two candidates for the possible domain structure in CCTO: antiphase boundaries separating regions in which the identity of the Ca sublattice is shifted by a primitive lattice vector, and twin boundaries separating domains in which the sense of rotation of the oxygen octahedra reverses. Actually, the PDF analysis could find the evidence of the Ca/Cu chemical disordering.

If such domain boundary exists, they could possibly give rise to a large dielectric response by so-called Maxwell-Wagner effect [10]. Owing to the oxygen deficiency, CCTO actually has a weak bulk conductivity. The conductance of the CCTO as a whole is eliminated by the presence of insulating antiphase or twin boundaries that divide the sample into nonpercolating, conducting domains.

4. SUMMARY

Cubic perovskite oxide of CCTO was investigated by high-energy X-ray diffraction measurements. Although dielectric constant of CCTO depended on the sintering condition, the average structure of 1100°C-sintered and 1040°C-sintered CCTO was same. On the other hand, PDF analysis reveal the improvement of coherency of short-range order in the 1100°C-sintered CCTO. This finding indicates somewhat domain structure exists in CCTO. A large dielectric response can be explained by

Fig. 7. Experimental PDF of the 1040°C-sintered CCTO (solid line) compared with that of the 1100°C-sintered CCTO (circles). Arrow shows the nearest-neighbor bond length of Ti-O. The nearest-neighbor PDF peak of the 1040°C-sintered CCTO is broader than that of the 1100°C-sintered CCTO.

Maxell-Wagner effect by taking into account the domain structure.

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