THE EFFECT OF DIFFERENT POLYMORPHS TiO_2 RAW MATERIALS ON THE DIELECTRIC PROPERTIES AND MICROSTRUCTURE IN $CaCu_3Ti_4O_{12}$ CERAMICS

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$CaCu_3Ti_4O_{12}$ ceramics with different polymorphs of TiO_2 as starting materials were prepared by the conventional solid-state reaction technique. Their crystalline structure, microstructure and dielectric properties were systematically investigated. It has been found that all of the ceramic specimens prepared in the present study have a good polycrystalline structure, and no secondary phase is been found by XRD. However, large differences in dielectric properties and microstructure are observed in them: 1) the characteristic frequency of dielectric relaxation around 1 MHz in the CCTO ceramics prepared with rutile TiO_2 is much lower than that in those ceramics prepared with anatase TiO_2; 2) no matter dielectric properties or microstructure, the CCTO ceramics prepared with rutile TiO_2 are more sensitive to the sintering temperature than those ceramics prepared with anatase TiO_2.

INTRODUCTION

High dielectric-permittivity materials have many potential technological applications, such as in capacitance-based components like capacitors, resonators and filters. $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much attention in particular over the past few years because of the interesting unusual physical properties [1-11]. It exhibits the extremely large ε' values over 10^4 with weak frequency dependence below 1 MHz at room temperature and little temperature dependence between 100 and 380 K [1-3]. Usually, Within the measuring frequency range of 40 Hz ~ 110 MHz, only one single dielectric relaxation with the characteristic frequency around 1 MHz is seen at room temperature or below [2-6] whereas an additional one in low frequency region is also observed at high temperatures [7-10]. To date, the most widely accepted mechanisms to interpret the complicated dielectric properties are seemed to be that the dielectric relaxation in the low frequency range region to an electrode polarization effect due to the Schottky barriers formed at electrode-ceramic interfaces [11-13] and the other one in the high frequency region to an internal barrier layer capacitance (IBLC) effect associated with insulating grain boundaries and semiconducting grains [4, 5]. Furthermore, the experimental results show that the microstructure and dielectric properties of CCTO ceramics can be greatly affected by their preparation conditions [5, 7, 14-17]. However, no information on the effect of raw materials to their dielectric properties and microstructure could be found in the literature until now.

The selection of raw materials is the first step in preparing ceramics, and also is one of the important factors that affect the final properties of those ceramics. Both suitable raw materials and stable source of raw materials are very important no matter in industrial production or scientific research. Therefore, keeping $CaCO_3$ and CuO raw materials unchanged, the effect of different polymorphs TiO_2 raw materials on $CaCu_3Ti_4O_{12}$ ceramic dielectric properties and microstructure was studied in this paper. It is found that the CCTO ceramics prepared with different polymorphs TiO_2 raw materials exhibit large difference in their dielectric properties and microstructure.

EXPERIMENTAL

CCTO ceramic were prepared by the conventional solid-state reaction technique, using raw materials of $CaCO_3$ (Shanghai Sinopharm Chemical reagents Co., Ltd., 99.0 %) CuO (Shanghai Sinopharm Chemical reagents Co., Ltd., 99.0 %) and two types of TiO_2 (A: Shanghai Sinopharm Chemical reagents Co., Ltd., 98.0 %,; B: Shanghai LingFeng Chemical Reagent Co., Ltd., 99.0 %). Raw materials were weighed according to stoichiometric ratio, mixed for 12 h in a ball mill with ZrO_2 balls and ethanol media, and calcined at 950°C for 4 h. Calcined mixture was then again ball-milled for 12 h and uniaxially pressed into pellet disks (with the dimension of 15 mm in diameter and 1.5 mm in thickness) at 180 MPa. Sintering was performed at 1050°C and 1080°C for 6 h in ambience.

Crystalline structures were investigated by X-ray diffraction (XRD) with CuKα radiation on a MSAL–XD2 diffractometer, and microstructures were examined with a HITACHI S-520 scanning electronic microscope (SEM). For electrical characterization, the ceramics were coated with silver paint and fired at 575°C for 20 min. Dielectric dispersions were measured by an Agilent 4294A impedance analyzer over the frequency range of 40 Hz ~ 110 MHz at room temperature.

RESULT AND DISCUSSION

There are three polymorphs (anatase, rutile and brookite) TiO_2 powder in the nature, and those mainly used in industrial production are anatase and rutile powder. Figure 1a) presents XRD profiles of A and B TiO_2 raw materials. By comparing with the XRD standard pattern, we can see that the polymorphs of A and B are anatase and rutile, respectively. (So the anatase and rutile powder are abbreviated hereafter as A and R in the following figures, respectively.) In order to compare the activity of anatase and rutile TiO_2 powder, heat-treating was performed to both TiO_2 raw materials at 750°C for 2 h. The XRD profiles of them after thermal treatment were shown in Figure 1b). The polymorph of anatase TiO_2 has become to rutile completely. The result indicates that the anatase TiO_2 exhibits higher reactivity.

Figure 2 gives XRD profiles of different CCTO ceramics prepared with both TiO_2 raw materials. Apparently, all these specimens reveal the quite similar diffraction profiles. The diffraction peaks could be indexed by a body-centered cubic perovskite-related structure of space group Im3 and no secondary phase appears within the detecting limitation of our XRD apparatus. It indicates that all of the ceramic specimens prepared in the present study have a good polycrystalline structure.

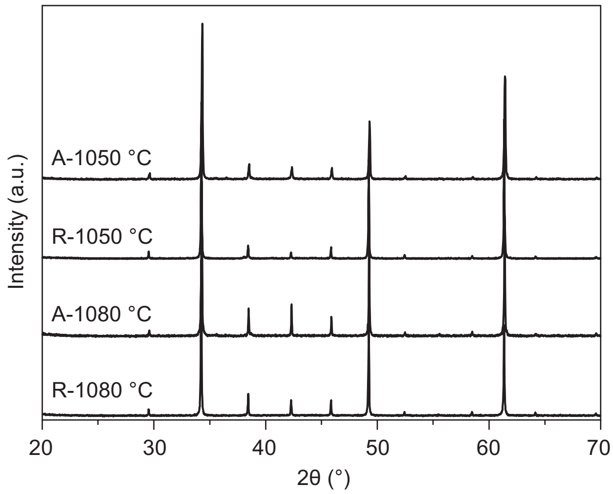
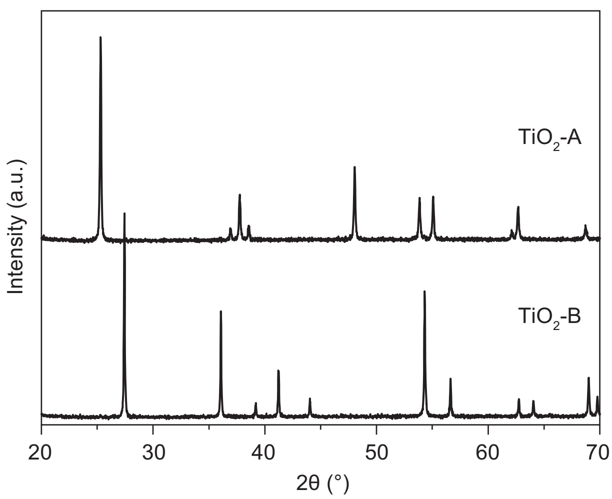
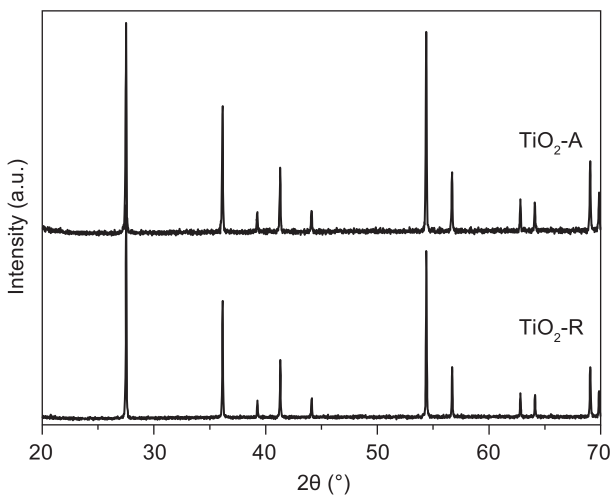


Figure 2. XRD profiles for different CCTO ceramics.

Figure 3 delineates the real and imaginary parts of dielectric dispersion for various CCTO ceramic specimens, measured at room temperature over the frequency range of 40 Hz ~ 110 MHz. From Figure 3a), it is clear that all of the specimens exhibit the giant dielectric permittivity at low frequencies, and the dielectric permittivity is almost independent of frequency below 100 kHz. Moreover, drastic decreases in the real parts of dielectric spectra are seen in the frequency range above 100 kHz, being accompanied by the appearance of



a) prime powder

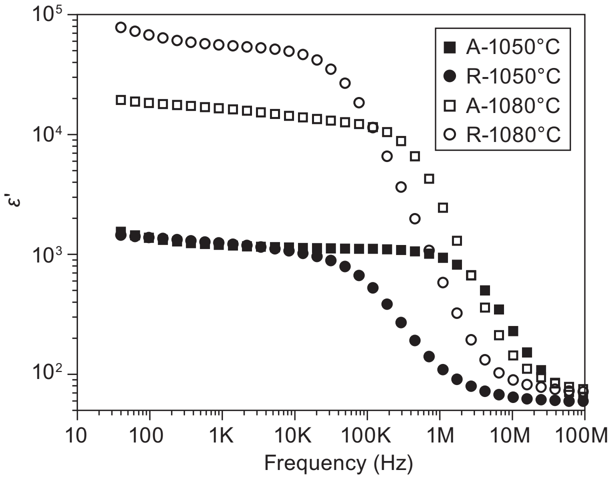


b) further thermally treated powder

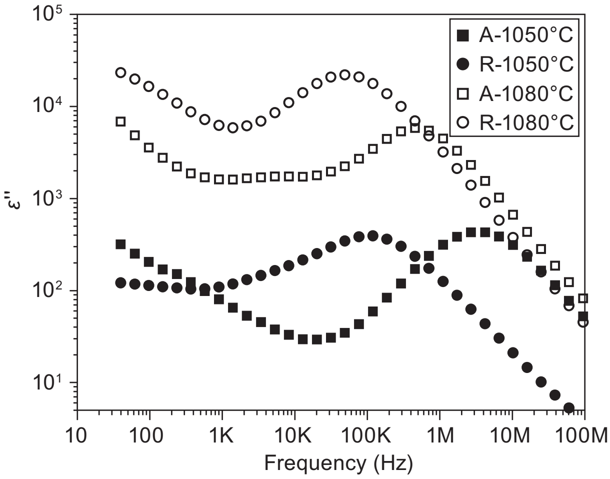
Figure 1. XRD profiles for different TiO_2 raw materials.

corresponding peaks in the imaginary parts of dielectric spectra, as shown in Figure 3b). The dielectric relaxation is Debye type, and these results agree well with that previously reported in the literature [4, 5, 7, 14]. Moreover, the dielectric permittivity of CCTO specimens prepared by two types of TiO_2 raw materials increases with the sintering temperature at room temperature. Observably, the characteristic frequencies of dielectric dispersion around 1 MHz in the ceramics prepared with rutile TiO_2 raw materials are much lower than those in the ceramics prepared with anatase TiO_2 raw materials; and the sensitivity of the dielectric properties to the sintering temperature in the ceramics prepared with rutile TiO_2 raw materials is stronger than that in the ceramics prepared with anatase TiO_2 raw materials.

As noted above, the microstructure of CCTO ceramics can be greatly affected by its preparation conditions [5, 7, 14-17]. The microstructure of CCTO ceramics will exhibit small grain size (1 ~ 30 μm) distribution, bimodal grain size (the large grains are about 60 ~ 100 μm, and small grains are about 3 ~ 5 μm) distribution, and then very large grain size (100 ~ 150 μm) distribution with the sintering temperature [14]. Figure 4 demonstrates the SEM images of fractured cross sections for the different CCTO ceramics. Comparing Figure 4a) and Figure 4b), the grain size of CCTO ceramics prepared by two types of TiO_2 raw materials at 1050°C exhibits significant

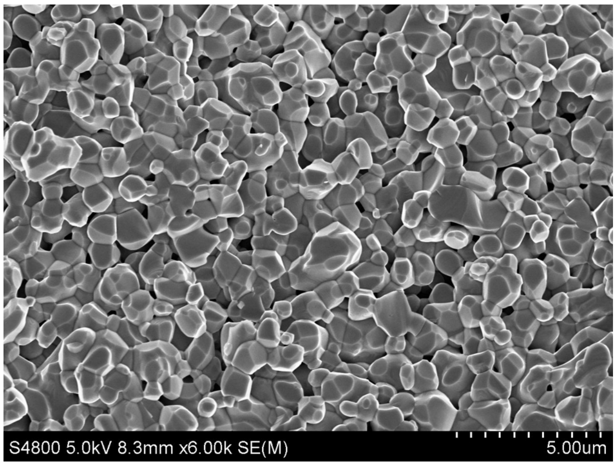


a) the real part ε'

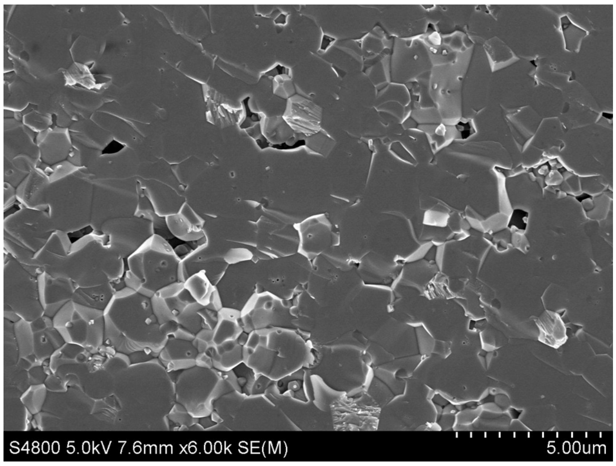


b) fthe imaginary part ε''

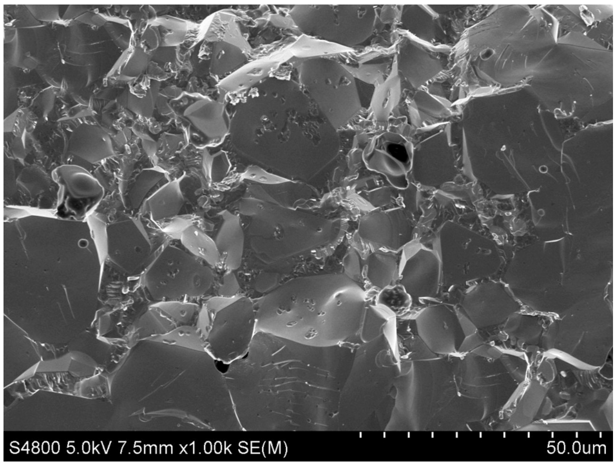
Figure 3. Dielectric dispersion curves of different CCTO ceramics measured at room temperature.



a) A-1050°C

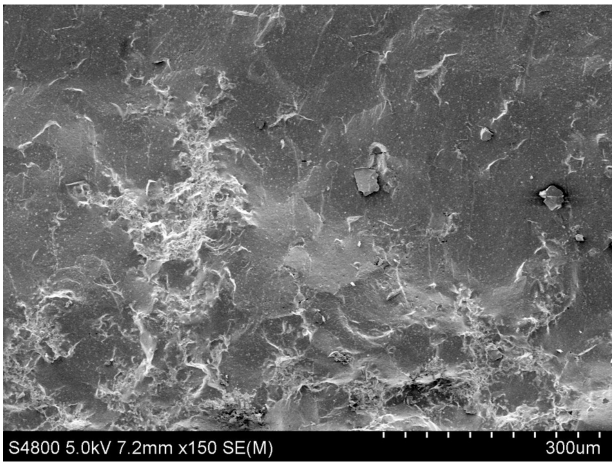


b) R-1050°C

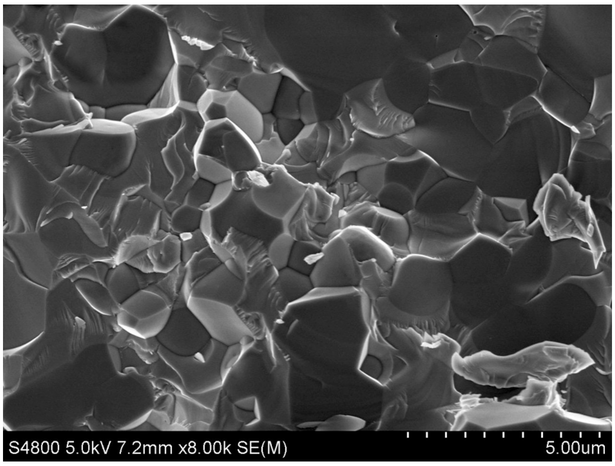


c) A-1080°C

Figure 4. SEM images of fractured cross-section microstructures for different CCTO ceramics.



d) R-1080°C



e) is the partial enlargement of (d)

Figure 4. SEM images of fractured cross-section microstructures for different CCTO ceramics.

differences: the grain size of the ceramics prepared with anatase TiO_2 raw materials is about 1 μm; while that of the ceramics prepared with rutile TiO_2 raw materials reaches 3 μm, which is significantly larger than that of the ceramics prepared with anatase TiO_2 raw materials. In the Figure 4c) and Figure 4d), the grain size of CCTO ceramics prepared with anatase TiO_2 raw materials at 1080°C is about 20 ~ 30 μm; however, there exist two classes of different grain sizes in the CCTO ceramics prepared with rutile TiO_2 raw materials at 1080°C: One class has the grain sizes of several micrometers, and the other has the large grain sizes in the order of several hundreds of micrometers. Generally, the result suggests that the sensitivity of the microstructure to the sintering temperature in the ceramics prepared with rutile TiO_2 raw materials is stronger than that in the ceramics prepared with anatase TiO_2 raw materials.

In our previous study, we have found that the dielectric properties and complex impedance of CCTO ceramics are intimately related to the microstructure and proposed an equivalent circuit model to interpret the experimental results.[7, 14] It contains three *RC* elements (R_xC_x, $R_{gb}C_{gb}$ and R_gC_g, respectively) and a frequency-dependent term Z_{UDR}. $R_{gb}C_{gb}$ represents the contribution of grain boundaries, R_gC_g describes the contribution of grains and R_xC_x delineates the contribution from an electrode polarization effect due to Schottky barriers formed at the electrode–ceramic interfaces, [11-13] respectively. Furthermore the dielectric relaxation at high frequencies in the dielectric dispersion spectra of the CCTO ceramics is caused by the IBLC effect associated with insulating grain boundaries and semiconducting grains [7, 14] and the other one in the low frequency range at high temperatures originates from an electrode polarization effect [11-13].

CONCLUSION

Various CCTO ceramics were prepared by the conventional solid-state reaction technique by using different polymorphs TiO_2 raw materials. Their crystalline structure, microstructure and dielectric properties were studied in detail. The results show that:

1) The characteristic frequencies of dielectric dispersion around 1 MHz in the ceramics prepared with rutile TiO_2 raw materials are much lower than those in the ceramics prepared with anatase TiO_2 raw materials.
2) No matter dielectric properties or microstructures, the sensitivity to the sintering temperature in the ceramics prepared with rutile TiO_2 raw materials is stronger than that in the ceramics prepared with anatase TiO_2 raw materials.

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