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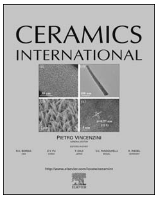

Low temperature preparation of $CaCu_3Ti_4O_{12}$ ceramics with high permittivity and low dielectric loss

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ABSTRACT

Low temperature preparation of $CaCu_3Ti_4O_{12}$ ceramics with large permittivity is of practical interest for cofired multilayer ceramic capacitors. Although $CaCu_3Ti_4O_{12}$ ceramics have been prepared at low temperatures as previously reported, they have rather low permittivity. This work demonstrates that $CaCu_3Ti_4O_{12}$ ceramics can not only be prepared at low temperatures, but they also have large permittivity. Herein, $CaCu_3Ti_4O_{12}$ ceramics were prepared by the solid state reaction method using B_2O_3 as the doping substance. It has been shown that B_2O_3 dopant can considerably lower the calcination and sintering temperatures to 870 °C and 920 °C, respectively. The relative permittivity of the low temperature prepared $CaCu_3Ti_{4-x}B_xO_{12}$ ceramics is about 5 times larger than the previously reported results in the literature. Furthermore, the dielectric loss of the $CaCu_3Ti_{4-x}B_xO_{12}$ ceramics is found to be as low as 0.03. This work provides a beneficial base for the future commercial applications of $CaCu_3Ti_4O_{12}$ ceramics with large permittivity for the cofired multilayer ceramic capacitors.

1. Introduction

Since the first report of colossal permittivity in the perovskite-type $CaCu_3Ti_4O_{12}$ (CCTO) ceramics in 2000 [1], many research groups have intensively investigated this oxide [2–6]. Compared with the commercially used $BaTiO_3$ ceramics in the electronic industry, the permittivity of CCTO ceramics has a better stability with temperature over a wide temperature range [1]. Such a low temperature dependence of the permittivity for CCTO ceramics will provide it with an advantage over the conventional $BaTiO_3$ ceramics in practical applications.

After over a decade of extensive studies on CCTO ceramics, the commercial application aspects of this material start to attract attention from researchers. One of the most important applications for colossal dielectric ceramics is the cofired multilayer ceramic capacitor (MLCC) application. In order to fabricate cofired MLCCs, a low temperature in the vicinity of 900 °C is usually required to cofire the dielectric materials with the Ag paste. CCTO ceramics are generally prepared by the conventional solid state reaction method using the raw materials $CaCO_3$, CuO, and TiO_2 [2–6]. This method is preferred for large scale production due to its simplicity and low cost. In order to prepare CCTO ceramics with the desirable dielectric properties, a relatively higher sintering temperature around 1080 °C is typically required [7–13]. However, this sintering temperature is too high for the cofired MLCC applications.

In order to lower the sintering temperatures of CCTO ceramics, researchers have employed compounds with low melting point as sintering aids [14–19]. CCTO powder is first synthesized by calcining the stoichiometric mixture of $CaCO_3$, CuO, and TiO_2. Sintering aids are mixed into the CCTO powder, and the mixture is pressed into pellets which are then sintered to obtain the CCTO ceramics. Goswami and Sen [14] used P_2O_5 as the sintering aid to lower the sintering temperature of CCTO ceramics to 1000 °C, which, however, is still higher than the melting point T_m of Ag (T_m =960 °C). Obviously, this is not suitable for the MLCC applications. Prakash and Varma [15] used B_2O_3 and $BaO–B_2O_3–SiO_2$ glasses as the sintering aids and lowered the sintering temperature to 950 °C. However, they only [15] obtained a quite low relative permittivity at about 350 at 1 MHz, and the dielectric loss was high. Wang *et al.* [16] used $SrO–B_2O_3–SiO_2$ glass as the sintering aid and lowered the sintering temperature from 1100 °C to 1050 °C, which also is too high for the MLCC applications. Löhnert *et al.* [17,18] used $Bi_2O_3–B_2O_3–SiO_2–ZnO$ glass as the sintering aid and lowered the sintering temperature of CCTO ceramics to 900 °C, and they fabricated MLCCs. However, the relative permittivity was also rather low, which is about 450 at 1 MHz [17,18]. Kulawik et al. [19] cofired CCTO MLCCs with Ag paste at 940 °C without using sintering aids. However, they obtained a quite low

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relative permittivity, which about 260 at 1 MHz [19].

In this work, instead of employing sintering aids to lower the sintering temperature of CCTO ceramics, we doped B_2O_3 into CCTO according to the formula $CaCu_3Ti_{4-x}B_xO_{12}$ (CCTBO). To synthesize the CCTBO, TiO_2 is partially substituted by B_2O_3 during the calcination stage, rather than adding B_2O_3 into CCTO powders during the sintering stage as in Ref. [15]. B_2O_3, with a low melting point (T_m =450 °C), is usually used in glass preparation for forming glass network and lowering the melting temperature of raw oxide materials. It is demonstrated that B_2O_3 dopant can considerably lower both the calcination temperature and the sintering temperature of CCTBO. In addition, the low temperature prepared CCTBO ceramics exhibit much better dielectric performance than the previously reported results [14–19]. This work provides a beneficial base for fabricating CCTO-based MLCCs with excellent dielectric performance.

2. Experimental

The raw materials for the CCTBO ceramics included $CaCO_3$ (99.99%), CuO (99.99%), TiO_2 (99.95%), and B_2O_3 (99.95%). The doping concentration x in the $CaCu_3Ti_{4-x}B_xO_{12}$ ceramics was chosen to be x=0, 0.02, 0.04, 0.06, 0.08. Stoichiometric mixtures of the raw materials were weighed and thoroughly ground. The ground powders were put in alumina crucibles, and then calcined in air in a box furnace at 870 °C for 10 h. After being ground, the powders were calcined again at 870 °C for 10 h. The calcined powders were thoroughly ground, and pressed into pellets with a diameter about 10 mm and a thickness about 2 mm under a uniaxial pressure of 200 MPa. The pellets were then placed in a box furnace, and sintered in air at 920 °C for 12 h. The samples were then naturally cooled down with the furnace to room temperature. For comparison, a pristine CCTO ceramic was prepared using the conventional processing conditions. In brief, the conventional calcination was done at temperature 1000 °C for 10 h, and it was conducted twice. The conventional sintering process was performed at 1080 °C for 12 h. Density of the CCTBO ceramics was measured using the Archimedes' method. For the measurements of their dielectric properties, the CCTO ceramics were polished and ultrasonically cleaned, and silver paste was printed on the CCTO ceramics. After being dried at 150 °C for 20 min, the CCTO ceramics were briefly heated at 600 °C for 15 min to obtain the silver electrodes.

The crystal structures of the CCTBO ceramics were analyzed using the X-ray diffraction (XRD, Bruker D8 Focus, CuK_α) technique, and their microstructure characteristics were observed on the freshly fractured surfaces with the scanning electron microscopy (SEM, Hitachi S-3000). The dielectric properties were measured using an Agilent 4284 A Precision LCR meter operated between 20 Hz and 1 MHz. All measurements were conducted at room temperature.

3. Results and discussion

3.1. Microstructural characteristics

Fig. 1a shows the XRD patterns of the calcined CCTBO samples. For the undoped CCTBO sample (x=0), the primary phase is CCTO, but some secondary phases, such as TiO_2, CuO and $CaTiO_3$, can be notably observed. This should be because the calcination temperature (870 °C) in this work is much lower than that generally used by other researchers. In the literature [20,21], the calcination temperature for CCTO is typically in the vicinity of 1000 °C. For the B_2O_3-doped samples (CCTBO, x=0.02, 0.04, 0.06, 0.08), it can be seen in Fig. 1a that the diffraction peaks for the secondary phases are much weaker. This suggests that the amount of secondary phases in the doped CCTBO samples is much less than in the undoped sample. Hence, B_2O_3 dopant enhances the solid state reaction process of CCTO. This should be because that B_2O_3 has a low melting point and it becomes liquid phase during calcination. The presence of liquid phase in calcination can significantly promote atomic diffusion and therefore enhances the solid state reaction process [22]. Fig. 1b shows the XRD patterns of the sintered CCTBO ceramics. For the undoped CCTBO ceramic, the presence of secondary phases, including TiO_2, CuO and $CaTiO_3$, is still notable. However, the doped CCTBO ceramics were almost free of secondary phases, although the two CCTBO ceramics with x=0.06 and 0.08 had very tiny traces of TiO_2 phase. In agreement with the results for the calcined CCTBO samples, the addition of B_2O_3 greatly promoted the solid state reaction.

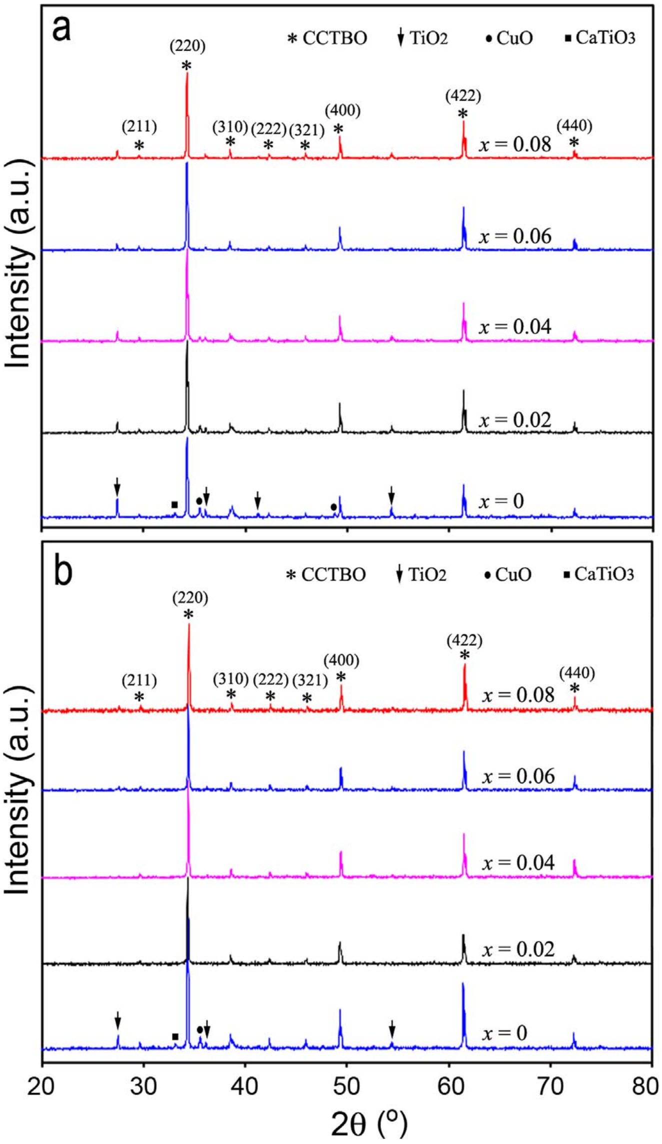

Fig. 1. XRD patterns of the CCTBO samples after the calcination (a) and after the sintering process (b).

The microstructures of the low temperature sintered CCTBO ceramics are shown in Fig. 2a to e. As shown in Fig. 2a, the undoped CCTBO ceramic contained only small grains with a diameter about 1–2 µm. This indicates that the atomic diffusion and grain growth were not complete for the undoped CCTBO ceramic during the sintering process at 920 °C. The reason should be because that the sintering temperature is too low for the undoped CCTBO ceramic which typically needs to be sintered at about 1080 °C [7–13]. For the doped CCTBO ceramic with x=0.02 (Fig. 2b), it contained both small and large grains, and the number of small grains was much less than the undoped sample (Fig. 2a). The shape of the small grains in the CCTBO (x=0.02) ceramic (Fig. 2b) was spherical-like, and they also had a larger diameter. The large grains in Fig. 2b had a diameter about 5~7 µm.