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Letter

An effective way to tune the microstructure and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics

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ABSTRACT

$CaCu_3Ti_{4-x}Mn_xO_{12}$ ($x \le 0.1$) ceramics has been prepared via the conventional solid-state method. The Mn substitution has strong effects on the microstructures and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics. The grain becomes obviously uniform and fine after a very small amount of Mn substitution for Ti. The intergranular phase gradually disappeares. The bulk resistivity increases from 10^7 to 10^9 Ω cm. Dielectric permittivity is abruptly suppressed to 10^2, and dielectric loss is significantly reduced to 10^{-3} for $x = 0.004$–0.04. The better microwave dielectric properties are also achieved for $CaCu_3Ti_{4-x}Mn_xO_{12}$ ($x = 0.004$) ceramics as follows: $\varepsilon_r = 68.1$, $Q \times f = 4030$ GHz, $\tau_f = 220$ ppm/K. These results suggest that a small amount of Mn substitutions for Ti is an effective way to tune the microstructure and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics.

1. Introduction

$CaCu_3Ti_4O_{12}$ (CCTO) has attracted considerable interest in view of its giant permittivity (10^4 to 10^5) in the frequency range from dc to 10^6 Hz, which suggests the potential application in capacitor based devices. And its giant permittivity is independent of temperature within a temperature range of 100–400 K [1–5]. A number of investigations have focused on the origin of the giant permittivity for CCTO [6–8]. Generally, the extrinsic effect is now accepted to be responsible for the giant permittivity. For CCTO ceramics, the origin of the giant permittivity is most attributed to an internal barrier layer capacitor (IBLC). Nowadays, intensive investigations suggest that IBLC is associated with semiconducting grains and insulating grain boundaries. However, using local current probing with atomic force microscopy, Fu et al. [8] clarify that the grain boundary displays semiconducting and the grain consists of semiconducting region and insulating region. There is much debate on the formation mechanisms of IBLC in CCTO ceramics. The IBLC model shows a nature of Maxwell–Wagner relaxation in CCTO ceramics. Unfortunately, the CCTO ceramics with giant permittivity exhibits higher dielectric loss and conductivity, which limits its practical applications. Therefore, some methods such as the substitutions and the insulating phase doping have been conducted to decrease the dielectric loss [9–12]. Some investigations show that the high permittivity and low loss have been achieved through substitution at some certain frequencies, such as $CaCu_{2.9}La_{0.2/3}Ti_4O_{12}$ ceramics with the high permittivity of 7500 and low dielectric loss less than 0.05 [9]. $CaCu_3Ti_4O_{11.7}F_{0.3}$ ceramics exhibits the giant permittivity over 6000 and low dielectric loss below 0.075 [10]. The similar effects have been observed in $CaTiO_3$, $SrTiO_3$ doped CCTO ceramics [11,12]. However, the dielectric loss is still not below 10^{-2}, and obviously increases with the frequency above 100 kHz. So it is too high for high-frequency applications.

For CCTO ceramics, the particular microstructure is observed by many researchers [2,3,5–8], which is associated with the IBLC. The melting phase, identified as CuO-rich phase, has been observed in the grain boundary of CCTO ceramics [2,13]. This suggests that the CuO-rich liquid phase appears during the sintering of CCTO based ceramics, which induces the abnormal grain growth. Due to the melting point of CuO beyond 1100 °C, therefore, the liquid phase may be the CuO–TiO_2 eutectic phase with low melting temperature of 919 °C in O_2 or 1020 °C in air [14,15]. If it is true, the tuning of CuO and/or TiO_2 stoichiometry will result in the significant variation of microstructure of CCTO, even the disappearance of IBLC homogeneous microstructure. This can be explained as following. Once the content of TiO_2 decreases, the CuO–TiO_2 phase shifts to CuO side. Therefore, the temperature corresponding to liquid phase elevates and liquid phase obviously decreases according to the CuO–TiO_2 phase diagram and the level rule [14,15]. Compared to the substitution for Cu, the smaller amount of substitution for Ti can be obtained the equivalent effect, as CuO–TiO_2 eutectic composition is close to CuO end.

This effect has been confirmed by Cu deficiency CCTO ceramics, which displays the microstructure of small and uniform grain sizes [5]. Kobayashi and Terasaki [16] has been previously reported the unusual impurity effects in the Mn substituted CCTO ceramics.

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Only 2 at% Mn substitution for Cu, the giant permittivity of CCTO ceramics dramatically drops down to 100. The similar effect is also confirmed by Sinclair and co-workers [17]. The Mn substituted CCTO ceramics of $CaCu_{2.85}Mn_{0.15}Ti_4O_{12}$ exhibits the following microwave dielectric properties of $\varepsilon \sim 93$, Qf ~ 3950 GHz and the temperature coefficient of resonant frequency $\tau_f \sim +657$ ppm/K [17].

Thus, based on the above analysis, a small amount of Mn substitution for Ti has been carried out to tune the microstructure and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics in the present work. It has been found that the microstructure varies from the huge grain to uniform and small grain. On the other hand, the permittivity and dielectric loss have been significantly suppressed. And the mechanism of microstructure evolution and electrical variations has also been discussed.

2. Experimental procedure

$CaCu_3Ti_{4-x}Mn_xO_{12}$ (x = 0, 0.001, 0.004, 0.01, 0.04, 0.1, hereafter referred as CCTMO) ceramics were prepared by solid-state reaction route. High purity $CaCO_3$, TiO_2, CuO and MnO_2 were weighed according to the stoichiometry and ball milled in distilled water using ZrO_2 milling media for 8 h. The slurry was dried and calcined at 950 °C for 6 h. The powders were ball milled again for 8 h, then dried and mixed with 10 wt% PVA for being uniaxially pressed into pellets (Ø 10 mm × 2–4 mm) under 100 MPa. These discs were sintered at 1060–1080 °C in air for 3 h.

The densities of the sintered pellets were measured with Archimedes method. The phase of the sample were identified by using X-ray diffraction (X'Pert Pro MPD, CuKα, λ = 0.15406 nm). The surface microstructure was observed by the environmental scanning electron microscope (ESEM, Philips XL30 ESEM-TMP). The samples were polished until the faces became plane and parallel. Silver electrodes were coated on the ceramics faces for dielectric measurements. Dielectric properties and impendence spectra were measured through a precise LCR meter (Agilent 4284A) at frequency range of 20 Hz to 1 MHz. The microwave dielectric properties of the specimens were measured by the TE01δ resonant mode using a network analyzer (Agilent E8361A).

3. Results and discussions

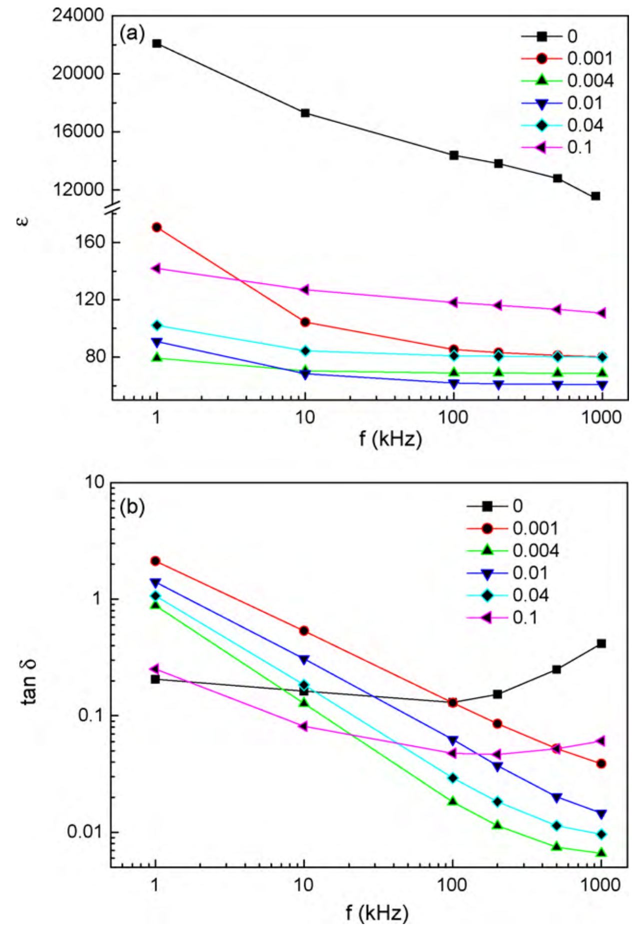

Fig. 1. Frequency dependence of permittivity (a) and loss (b) for $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics.

Fig. 1 shows the dielectric permittivity and loss tangent of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics at room temperature within the frequency range from 1 kHz to 1 MHz. As previous investigations [5–10], the giant permittivity above 10,000 is obtained for undoped CCTO over the whole frequency range. The permittivity of CCTMO ceramics abruptly drops to 10^2 with a very small amounts of Mn substitution, i.e. x = 0.001. It is noted that the permittivity is insensitive to frequency. Meantime, the loss tangent of CCTMO ceramics obviously decreases, which is effectively suppressed to 10^{-2} to 10^{-3} at 1 MHz. For the ceramics with x = 0.004, the loss tangent reaches the lowest value of 0.005. On the other hand, the permittivity of the present ceramics decreases firstly with Mn content increasing, then a little elevates. These results indicate that Mn substitution on Ti-sites has a remarkable effect on the dielectric properties for CCTO ceramics. The similar phenomena are also reported by some other previous works [16,18], which have not mentioned the effect on dielectric loss. However, a very small Mn substitution on Ti-sites has a significant difference from the large amount of Mn substitution reported by Makcharoen et al. [19]. They have reported that high permittivity ($\varepsilon > 1200$) and low dielectric loss ($\tan\delta < 0.06$) for $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics with x = 0.24.

Fig. 2 illustrates the temperature variations of the dielectric properties of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics. It is obvious that the Mn substituted ceramics displays better thermal stability than the pure CCTO ceramics. The permittivity of CCTMO ceramics is relatively independent of temperature. Within the investigating composition range, CCTO ceramics has the lager positive temperature coefficient of permittivity (τ_ε = 2493 ppm/°C at 1 MHz); then very small amount of Mn substitution (x = 0.001) significantly suppress temperature coefficient to low value of 625 ppm/°C. On the other hand, negative temperature coefficients of permittivity are observed for further increase of Mn substitution, which are −546 ppm/°C, −437 ppm/°C, −525 ppm/°C for x = 0.004, 0.01, 0.04, respectively. When x increases to 0.1, permittivity linearly increases with elevating temperature, and τ_ε is equal to 673 ppm/ °C. As shown in Fig. 2(b), $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics x = 0.004–0.01 exhibits a low dielectric loss ($\tan\delta \sim 10^{-3}$), which is insensitive to temperature below 60 °C. However, as the temperature goes up, the loss tangent value increases rapidly.

X-ray diffraction patterns of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics are shown in Fig. 3. All diffraction peaks agree well with CCTO phase (ICDD No. 75-2188). This suggests that the CCTO based solid solution is formed in CCTMO ceramics. Fig. 4 exhibits SEM images of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics. The microstructure with the large grain and intergranular phase uniform is observed in CCTO ceramic, which is reported in some literatures [20,21]. For x = 0.001, a bimodal distribution of grain size appears, the small grain of several micrometers distributes among the large grain with several tens of micrometers. This similar microstructure is also observed in the CCTO ceramics sintered at the lower temperature [20,21]. With the increase of Mn substitution, the CCTMO ceramics with x = 0.004 and 0.1 exhibits the dense microstructure with the small and uniform grain, the large abnormal grains disappear. The evolution of microstructure in the CCTMO ceramics is attributed to the variation of CuO-rich liquid phase, which is believed to form in the CCTO ceramics during the sintering. As stated in introduction, the liquid phase may be the CuO–TiO_2 eutectic phase with low melting temperature. With the small amount of Mn substitution for Ti, the CuO–TiO_2 system will shift to CuO side far from the eutectic composition point. Therefore, the temperature corresponding to

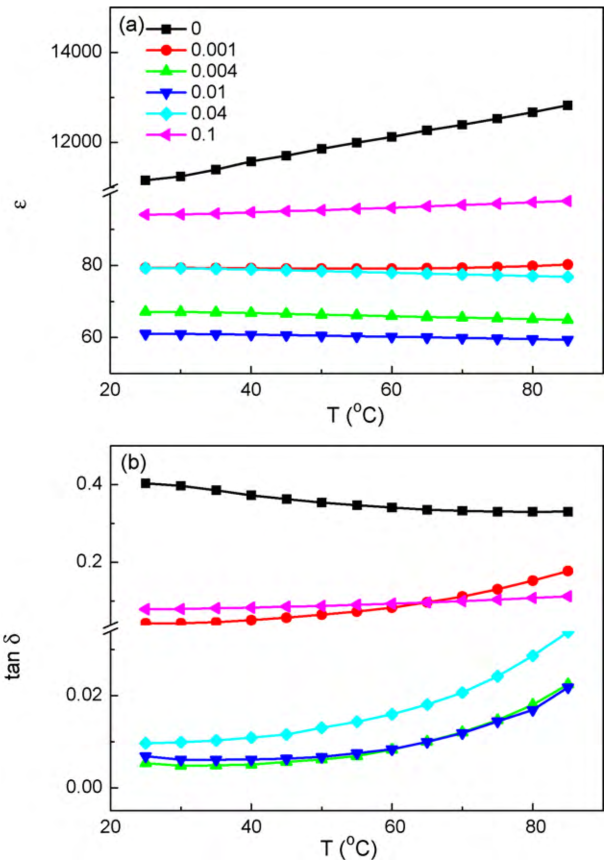

Fig. 2. Temperature dependence of permittivity (a) and loss (b) for $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics at 1 MHz.

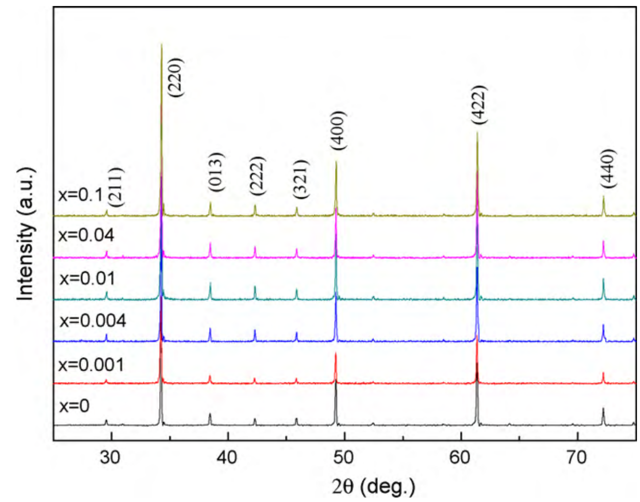

Fig. 3. XRD pattern of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics.

the liquid phase elevates at a certain extent. On the other hand, the CuO-rich liquid phase would decrease according to the level rule. It is confirmed by the microstructure evolution of CCTMO ceramics with the different Mn content. The microstructure varies from the coexistence of large grain and intergranular phase for $x = 0$ to the small and uniform grain for $x = 0.1$.

To better understand the microstructure evolution, the complex impedances of the CCTMO ceramics are also measured as shown in Fig. 5. Two semicircular arcs in the complex impedance plane are evidently observed for all the specimens, which agree with those reported in the literatures [1,3]. The complex impedance can be explained by an equivalent circuit of two parallel RC elements connected in series, of which one RC element is corresponding to the

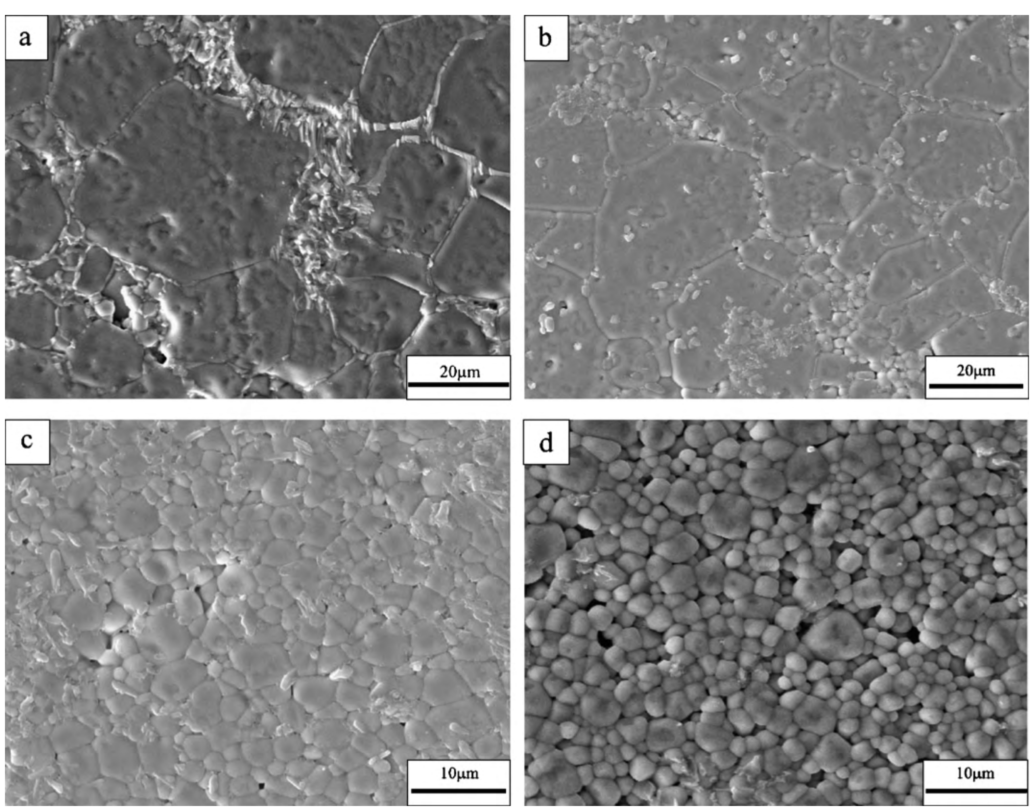

Fig. 4. SEM images of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics (a) $x = 0$; (b) $x = 0.001$; (c) $x = 0.004$; (d) $x = 0.1$.

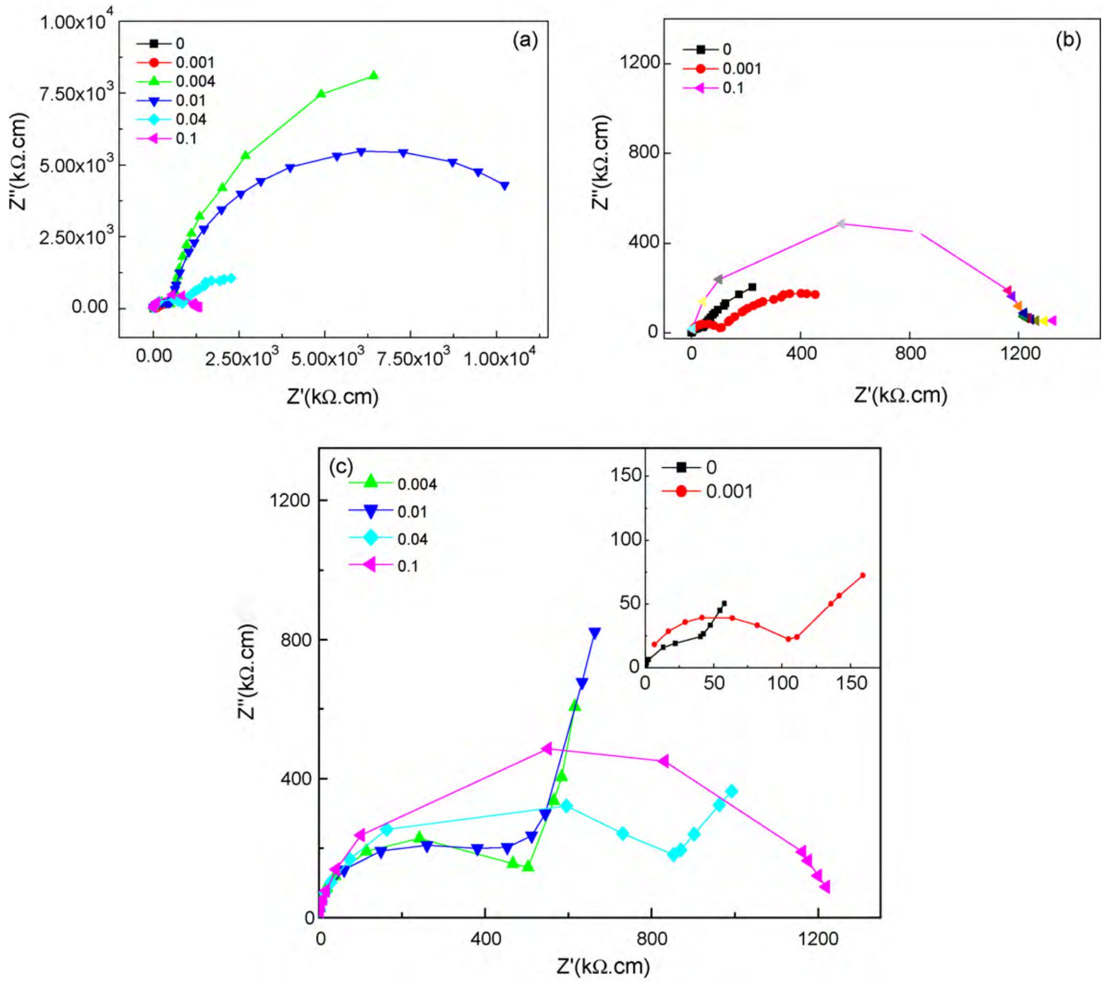

Fig. 5. Complex impedance plots of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics (a), expanded views (b) for $x = 0$, 0.001 and 0.1; (c) the high-frequency complex impedance data, the inset shows expanded graph when $x = 0$ and 0.001.

semiconductive region and the other one is corresponding to insulate region. Both the low frequency and the high frequency, the resistivity increases up to $x = 0.004$ with Mn content increase, then decreases with further increase of Mn content. It is worth noting that the magnitude of resistivity increases up to three orders with a very small Mn substitution for Ti. This indicates that Mn substitution has significant enhance effect on the resistivity of CCTO ceramics. So it suggests that the intergranular phase may be the semiconductive region.

DC resistivity of CCTMO ceramics measured at room temperature is also shown in Fig. 6. The curve is quite coincidence with the result demonstrated in Fig. 5. The resistivity of Mn substituted CCTO ceramics is improved from 10^7 to 10^9 Ω cm. As stated above, the small amount of Mn substitution on Ti-sites suppresses the CuO-rich liquid phase. Therefore, as seen in SEM images, the microstructure of small and uniform grain is obtained for Mn substituted CCTO ceramics. And the intergranular CuO-rich phase displays conductive behavior. So these result in the large increase of resistivity. Accompanying, the IBLC effect is greatly weakened, even disappears. As a result, permittivity is suppressed to about 70, which is similar to the permittivity of CCTO ceramics at low temperature (below 100 K) or the microwave frequency [6,21]. Especially, the dielectric loss is also effectively reduced. And microwave dielectric properties of CCTMO for $x = 0.004$ are $\varepsilon_r = 68.1$, $Q \times f = 4030$ GHz and $\tau_f = 220$ ppm/°C.

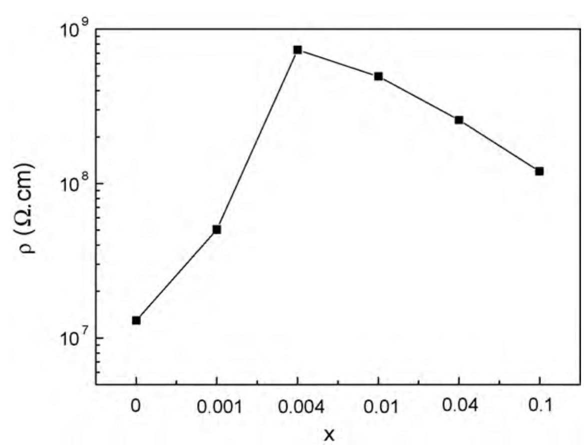

Fig. 6. DC resistivity of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ceramics at room temperature.

4. Conclusions

CCTO ceramics with a small amount of Mn substitution for Ti has been prepared by solid-state reaction method. It is found that Mn substitution for Ti is an effective way to tune the microstructure and dielectric properties of CCTO ceramics. CCTO based solid solution was formed in the Mn substituted CCTO ceramics. The microstructure varies from the large grains and an intergranular phase for CCTO ceramics to the small and uniform grains for Mn substituted CCTO ceramics. Resistivities of grains and grain boundaries can be evidently increased. The permittivity is suppressed to 10^2, and the dielectric loss is effectively reduced to 10^{-3} at 1 MHz. And the microwave dielectric properties of $CaCu_3Ti_{4-x}Mn_xO_{12}$ ($x = 0.004$) ceramics are $\varepsilon_r = 68.1$, $Q \times f = 4030$ GHz and $\tau_f = 220$ ppm/°C. It is potential application as high-ε and low temperature cofired ceramics.

Acknowledgements

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