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ORIGINAL PAPER

Microstructure and dielectric properties of Nd doped $CaCu_3Ti_4O_{12}$ synthesized by sol–gel method

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Abstract $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ($x = 0$, 0.1, 0.2 and 0.3) powders and ceramics were prepared by sol–gel method. Effect of Nd on microstructure and dielectric properties were investigated. XRD patterns suggest that pure perovskite-like CCTO phase were obtained after calcining at 800 °C for 2 h. SEM pictures reveal that particle size monotonously decreases from 250 to 120 nm with increase of Nd concentration. The lattice parameters show an increasing trend with the enhancing amount of Nd^{3+} substitution. The average grain size of CCTO ceramics decrease from 2.0 to 0.8 μm with increase in Nd doping, which indicates that high concentration of Nd inhibits grain growth of $CaCu_3Ti_4O_{12}$. Both of the dielectric constant and dielectric loss decrease with increase in Nd concentrations. $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ceramics with $x = 0.3$ shows the lowest dielectric constant of 1.12×10^4 as well as the lowest dielectric loss value of 0.12 at 20 °C(10 kHz).

Keywords $CaCu_3Ti_4O_{12}$ · Doping · Nd · Dielectric properties

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1 Introduction

High dielectric constant materials are useful for miniaturization of electronic devices. In this situation, calcium copper titanate ($CaCu_3Ti_4O_{12}$) has attracted a lot of interest in the past few years. This material exhibits colossal dielectric constant of $\varepsilon_r \sim 10{,}000$ with the temperature range 100–600 K [1–3]. Temperature independent colossal dielectric constant of $CaCu_3Ti_4O_{12}$ (CCTO) has drawn the attention of many researchers worldwide. But high dielectric loss (tanδ), low breakdown voltage and high leakage current have certainly become a barrier to its industrial applications [4]. Among the previous works, the internal barrier layer capacitor (IBLC) model, which considers CCTO as consisting of semi-conducting grains with insulating grain boundaries, has been widely accepted to describe the origin of the unusually high dielectric constant of CCTO [5–7]. This electrostatic barrier obstacles the current flow through the bulk semi-conducting grains in presence of an applied field resulting huge dielectric constant value.

It is known that the radius, valancy and coordination number of an element are important parameters to determine the site it occupies in the parent compound. Up to now, there are several reports on the giant dielectric properties of CCTO [8, 9] and related oxides of the type $ACu_3Ti_4O_{12}$ where A = Sr [10], Cd [11, 12], $La_{2/3}$ [13, 14]. Some doping ions can reduce significantly dielectric loss of CCTO ceramics. La^{3+} substitution into CCTO can reduce dielectric loss to be less than 0.03 [15]. Both Nb and Fe doping lowered the dielectric loss [16]. The dielectric loss at low frequencies ($f < 10^4$ Hz) in $CaCu_3Ti_4O_{12}$ could be reduced by adding $CaTiO_3$ and ZrO_2 [17, 18]. However, the reduction of dielectric loss is usually accompanied by a decrease in dielectric

constant value. Dielectric loss of CCTO is too high due to conducting crystalline grains/sub grains. The conductance of the barrier leads to the leakage loss. It has been revealed that addition of $CaTiO_3$ increases the resistance of the barrier layers [19, 20].

CCTO was generally prepared by the traditional solid-state method [1], which suffers from the disadvantages of tedious work, relatively long reaction times, high calcined temperatures and inhomogeneity [21]. In recent years, there were a lot of reports on the sol–gel processing to synthesize CCTO [22–24]. Compared with traditional solid-state method, the sol–gel method affords intimate and homogeneous mixing of the metal ions at the molecular scale, thus reducing the diffusion path length required. Shorter diffusion lengths lead to shorter reaction times and lower temperatures [23]. In addition, many different processing conditions can be selected in the sol–gel technique, such as reagent, solvent, temperature, etc. In this work, an attempt has been made to synthesize a few compositions in the $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ (CNCTO) by sol–gel method and study its microstructure and dielectric properties.

2 Experimental

All of employed chemicals were analytical reagent grade and supplied by ShangHai LingFeng Chemical Reagent Co. Ltd. $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ($x = 0$, 0.1, 0.2 and 0.3, designated as CCTO, $CNCTO_1$, $CNCTO_2$ and $CNCTO_3$, respectively) powders were prepared by sol–gel method. The weighted $Ca(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and $Nd(NO_3)_3{\cdot}6H_2O$ were dissolved into absolute ethyl alcohol and deionize water(the volume ratio of absolute ethyl alcohol to water = 3:1). Meanwhile, stoichiometric $Ti(OC_4H_9)_4$ liquids were dissolved into CH_3CH_2OH to form 0.5 M solution. Acetic acid was added to adjust the acidity of solution (pH 3) in order to form the gels slowly. Both above solutions were mixed with vigorous stirring. Amount of citric acid was added into the mixture and the blue gel was gradually formed. Subsequently, the gel was dried at 80 °C to obtain xerogels. Finally, the xerogels was calcined at 800 °C for 2 h to yield $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ powders.

The as-prepared powders were thoroughly pulverized in an agate mortar and pressed into discs of 10 mm in diameter at around 50 MPa and sintered at 1,000 °C for 6 h. After polishing, silver paste was used to coat both sides of sintered discs, and then fired at 600 °C for 10 min to form electrodes in order to measure dielectric properties.

The thermal decomposition characteristic of xerogel was investigated by TG/DSC (TG 209 F3, Germany) in air atmosphere with heating rate of 10 °C/min from 30 to 800 °C. The phase composition of the powders and the sintered ceramics were analyzed by X-ray powder diffraction (D/max 2,500 PC, Japan) using a Cu Kα radiation ($\lambda = 0.15406$ nm) form 20 to 80°. The microstructure of powders and ceramics was observed using SEM (JSM-6360LA, Japan) and energy dispersive spectroscopy (JSM-6360LA, Japan). The relative density of ceramics was measured by the Archimedes method. Dielectric properties of sintered ceramics were measured as a function of temperature using a LCR meter (AT821, China).

3 Results and discussion

TG/DSC was carried out on xerogel to study the thermal decomposition process. Figure 1 shows the representative TG/DSC plots of the precursor of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ with $x = 0.2$. It is observed that there are three stages of weight loss corresponding to an endothermic peak and two exothermic peaks in the temperature range up to 700 °C. The DSC curve appears a small endothermic peak at 192 °C, accompanied by about 26.6 % weight loss in TG curve, which resulted from the removal of absorbed water and solvent. At the elevating temperature, two exothermic peaks appear at 247 and 295 °C in DSC curve, accompanied by 16.9 and 7.7 % weight loss in TG curve, respectively, which may be due to the main decomposition of nitrates and organic groups. There is almost no weight loss in TG curve above 400 °C, which indicates non-crystalline oxides slowly reacted and transferred to polycrystallines.

To help understand the evolution of the powders, XRD patterns of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ for ($x = 0.2$) xerogels with different heat-treatment temperatures are shown in

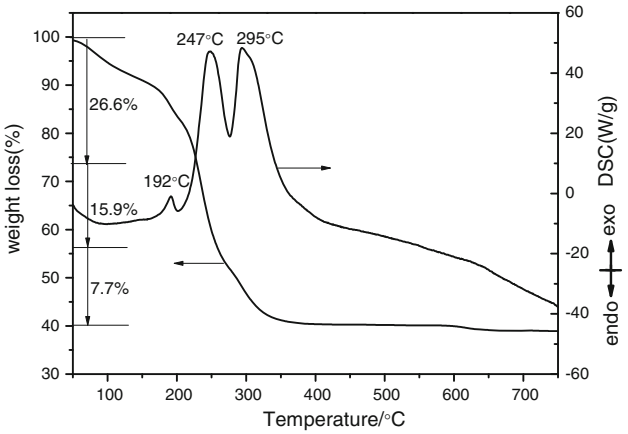

Fig. 1 TG/DSC plot of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ for ($x = 0.2$)

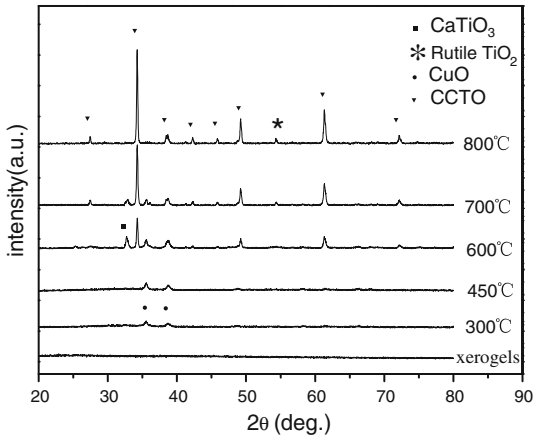

Fig. 2 XRD patterns of $CNCTO_2$ xerogels with different heat-treatment temperatures

Fig. 2. It can be seen in the figure that xerogels are amorphous without heat-treatment. The powders calcined at 300 °C shows the peaks corresponding to CuO. The diffraction peaks corresponding CCTO crystalline gradually appear and small amount of $CaTiO_3$ and CuO are also present in this stage when the calcination temperature increases to 600 °C. With the increase in the calcination temperature from 600 to 800 °C, the peaks of CCTO increase in intensity and the peaks corresponding to CuO and $CaTiO_3$ decrease and vanish completely when the calcinations temperature is 800 °C. This indicates that $CaTiO_3$ react with CuO to form CCTO powders above 600 °C. And we observed a small amount of rutile TiO_2 phase formation at 800 °C. No secondary phases containing Nd were detected because XRD is not sensitive to concentrations under 0.5 wt% [25]. The Nd^{3+} was most likely substituted in Ca lattice sites. These two occurrences are attributed to the lack of Nd found in the $CNCTO_2$ XRD spectra.

Figure 3 shows SEM photographs of pure and Nd doped CCTO powders at various levels after calcining at 800 °C for 2 h. SEM observation indicates that all samples exhibit a good dispersity with uniform particle size. It decreases to 120 nm for $x = 0.3$, from 250 nm for $x = 0$. It can be assumed that Nd has effect on CCTO particle size.

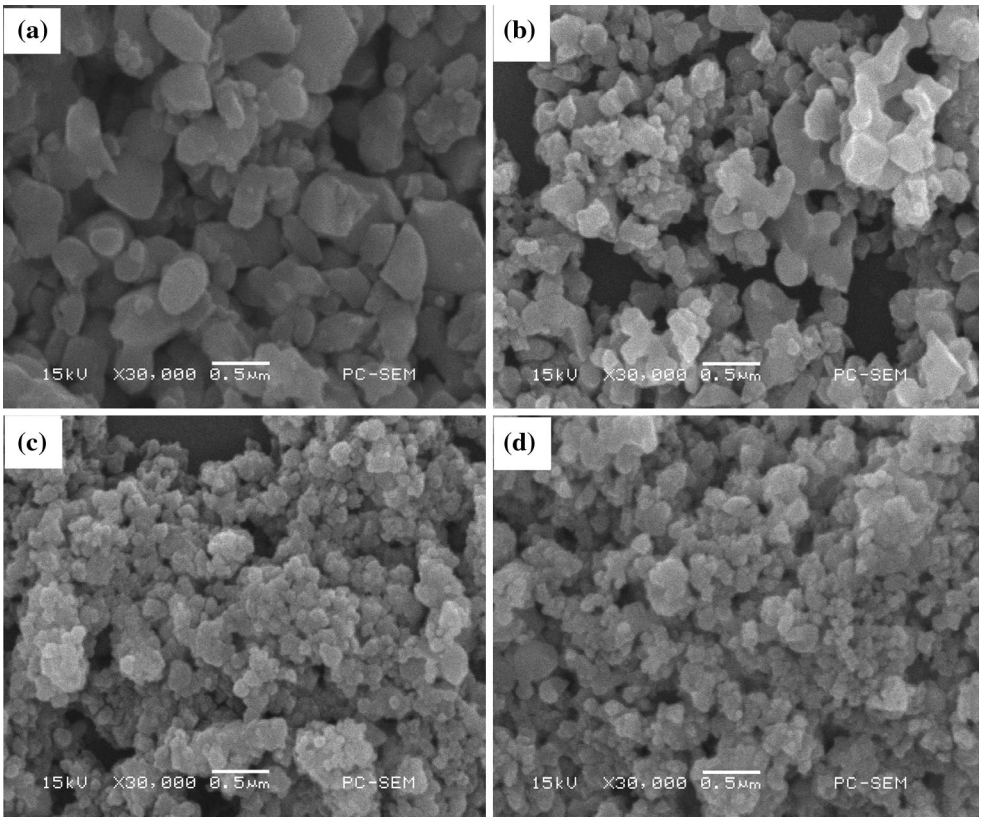

Fig. 3 SEM photographs of **a** CCTO, **b** $CNCTO_1$, **c** $CNCTO_2$, **d** $CNCTO_3$ powders

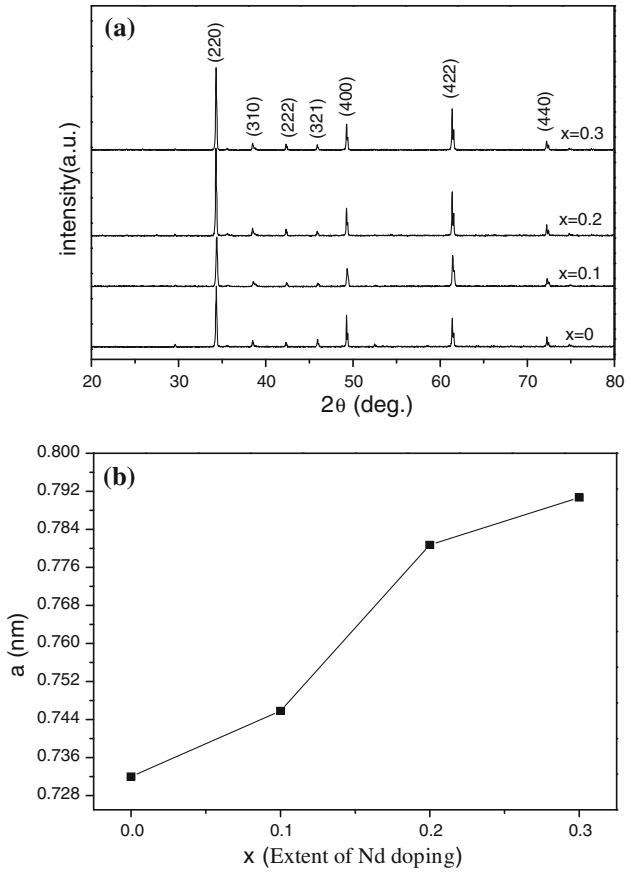

Fig. 4 **a** X-ray diffraction pattern of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ceramics, **b** Variation of lattice parameters with the extent of Nd doping

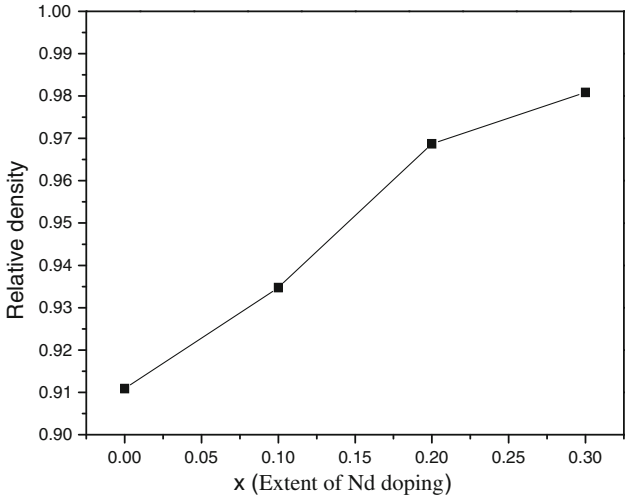

Fig. 5 Relative density of pure and Nd doped CCTO ceramics sintered at 1,000 °C for 6 h

Meanwhile, the particle size decreases with increase in dopant concentration, also reported by other authors for sol–gel methods [14].

X-ray diffraction patterns of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ (where $x = 0$, 0.1, 0.2 and 0.3) ceramics are shown in Fig. 4. Comparing these patterns with those of the standard powder XRD pattern of CCTO (JCPDS Card No.75–2188), the diffractogram shows that the sintered ceramics are polycrystalline and no secondary phase is formed for doping by Nd up to $x = 0.3$, leading to conclude that Nd^{3+} is replacing Ca^{2+} in its lattice position in the doped ceramics, without distorting the crystal structure. The lattice parameter was determined using least square refinement method show an increasing trend with the enhancing amount of Nd^{3+} substitution. It increases to 0.73907 nm for $x = 0.3$, from 0.7320 nm for $x = 0$. This lattice parameter enhancement with increasing amount of Nd^{3+} doping is expected since the ionic size neodymium (Nd^{3+}) is bigger than that of calcium (Ca^{2+}). This is called ionic size effect. Researchers have proved the existence of Ti^{3+} along with Ti^{4+} from the photoemission spectroscopy of CCTO [26]. Therefore this reduction of lattice parameter may also be due to increasing amount of Ti^{3+}, formed by reduction of Ti^{4+} to Ti^{3+} by Nd^{3+} due to its oxidizing property.

Figure 5 presents the variation of relative density of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ceramics as a function of Nd concentration. It can be seen that the relative densities increase as Nd concentration increase. $CNCTO_3$ ceramics shows the highest relative density of 98.1 %, which may be due to less pores and uniform particle size of powders. It is difficult to prepare fully dense ceramics due to a lot of factors which can affect on producing fine-grained materials with high density, such as powder preparation process, powder agglomeration and sintering conditions [27]. In addition, many researchers reported that dopants can also have effect on the densification and microstructure of perovskite [28].

Figure 6a, b, c presents SEM images of fracture surface for pure and Nd doped CCTO ceramics. It is clearly seen that microstructure of CNCTO ceramics changes significantly with increase in concentration of Nd. The average grain size becomes small with increase in Nd doping. Pure CCTO shows the average grain size about 2.0 μm, whereas for subsequent doping concentrations, the average grain size decreases to 0.8 μm for $CNCTO_3$ ceramics. This result indicates that Nd inhibits grain growth of CCTO ceramics.

Energy spectrum of elemental analysis performed on different regions of $CNCTO_3$ gives insight into the proportion of different elements in grain and grain boundary. It can be seen from Fig. 6d that Nd appears in the grain and

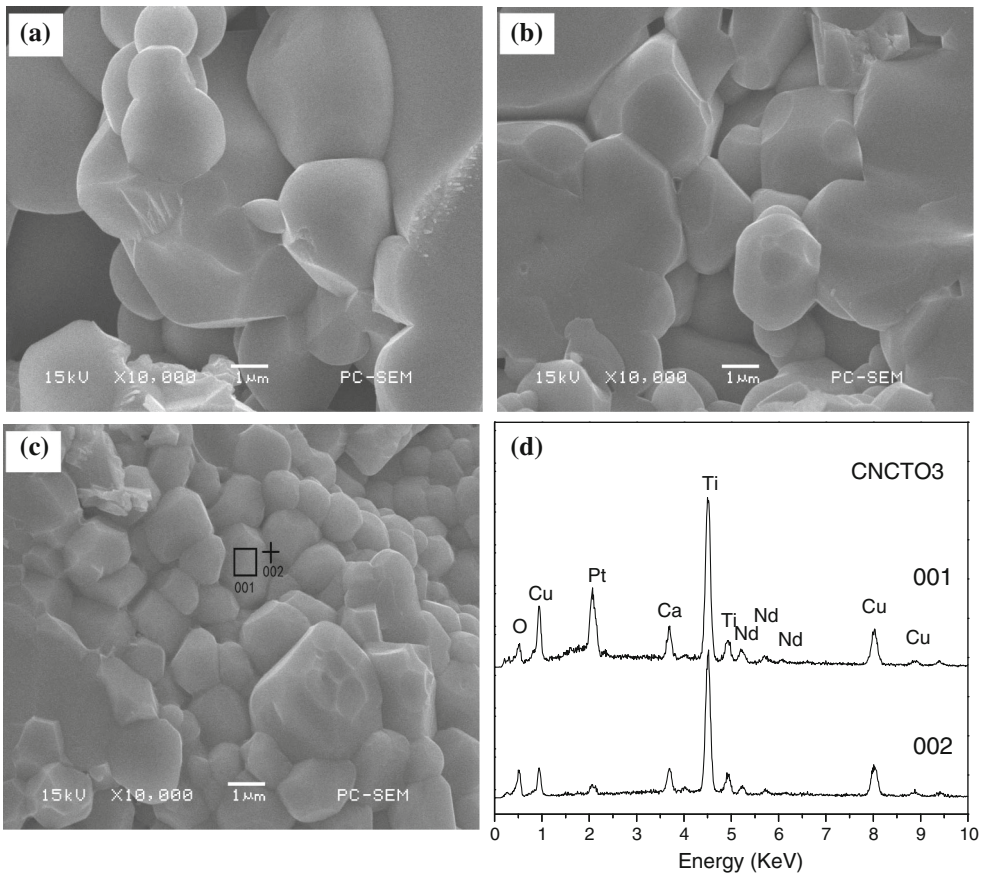

Fig. 6 SEM images of $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ceramics: **a** $x = 0$, **b** $x = 0.1$, **c** $x = 0.3$, **d** gives EDS analysis of CNCTO ($x = 0.3$) for different regions

grain boundary of $CNCTO_3$ as well as Ca, Cu, Ti, and O (the peaks of Pt were originated for conducting of specimen). Major content of Nd was found in grain (10.99 %) than in grain boundary region (9.57 %). Lesser Nd content in the grain boundary may be the major cause for the refinement in grain size [29].

Figure 7a illustrates temperature dependence of the dielectric properties for pure and Nd doped CCTO ceramics at the frequency of 10 kHz. The dielectric constant (ε_r) and dielectric loss ($\tan\delta$) increased continuously by increasing temperature, although the rate of these enhancements was not the same. It can be seen that the thermal stability of $CNCTO_2$ and $CNCTO_3$ is considerably higher than that of CCTO and $CNCTO_1$. It is obvious that the dielectric constant and dielectric loss was found to drastic decreases with increase in Nd dopant concentration. CCTO exhibits the highest dielectric constant (2.9×10^4) and dielectric loss (0.24) at 20 °C, while $CNCTO_3$ shows the lowest dielectric constant (1.12×10^4) and dielectric loss (0.12) at 20 °C. The results indicate that Nd doping can decrease dielectric constant as well as dielectric loss. According to the literature [30], the dielectric constant of $CaCu_3Ti_4O_{12}$ is closely related to its grain size, and larger grains result in higher dielectric constants for $CaCu_3Ti_4O_{12}$. Our results lead to the same conclusion, whereby with larger grain size, a larger dielectric constant was observed for pure CCTO. It can be easily understood with the internal barrier layer capacitor (IBLC) model, which consider materials consist of conducting grains and insulating grain boundaries. As a greater amount of crystal defects are able to exist in larger grains than that in smaller ones. Thus, there must be insulating planar defects in these grains. Dopants frequently concentrate at lattice defects. The Nd may be concentrating on the important planar defects in CCTO. This could increase the electrical resistivity of the internal barrier and decrease the dielectric loss.

4 Conclusion

Sol–gel method was employed to synthesize pure and Nd-doped $CaCu_3Ti_4O_{12}$ ceramics. XRD patterns shows that

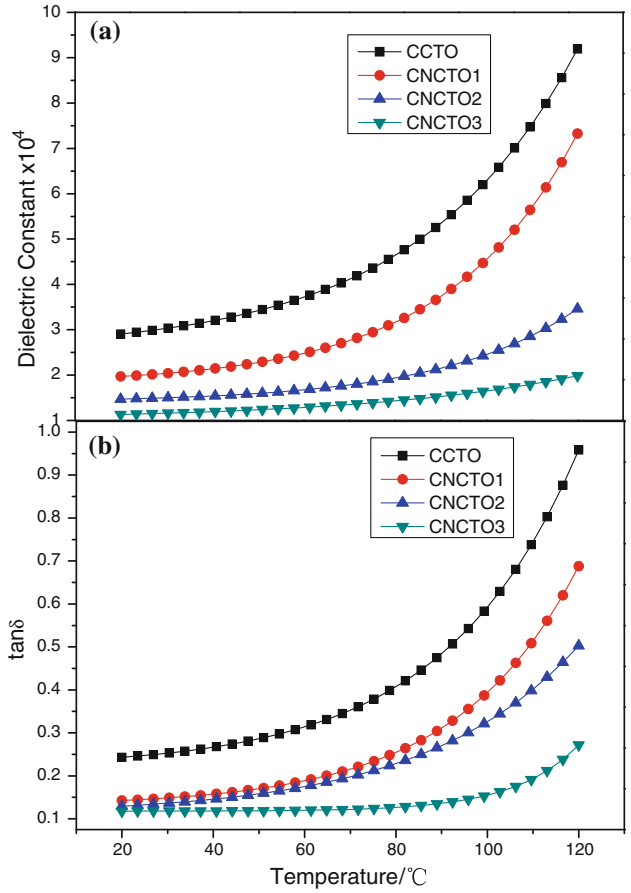

Fig. 7 Temperature dependence of dielectric properties for $Ca_{(1-3x/2)}Nd_xCu_3Ti_4O_{12}$ ceramics at the frequency of 10 kHz

CNCTO ceramics (sintered at 1,000 °C for 6 h) were single phase with no Cu-rich phase. The lattice parameters show an increasing trend with the enhancing amount of Nd^{3+} substitution. SEM graphs show that the particle size decreases with increase of Nd concentration. Dielectric constant and dielectric loss is found to decrease with the increase of Nd incorporation. $CNCTO_3$ ceramics exhibits the lowest dielectric constant of 1.12×10^4 as well as the lowest dielectric loss value of 0.12 at 20 °C (10 k Hz). Nd doping has obvious effects on grain growth and dielectric properties of CCTO ceramics.

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