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Effect of La-doping on the properties of $CaCu_3Ti_4O_{12}$ dielectric ceramics

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Abstract

Nano-size $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ (χ = 0.00, 0.05, 0.10, 0.15 and 0.20) precursor powders were prepared via the sol–gel method and the citrate auto-ignition route and then processed into micro-crystal $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics under heat treatment. Characterization of the as-obtained ceramics with XRD and SEM showed an average grain sizes of ~1–2 μm, indicating La^{3+} amount to have little impact on grain size. The room-temperature dielectric constant of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics sintered at 1000 °C was of the order of 10^3–10^4 despite the variation of χ values. Compared with $CaCu_3Ti_4O_{12}$, La^{3+}-doped $CaCu_3Ti_4O_{12}$ showed a flatter dielectric constant curve related to frequency. It was found that the loss tangent of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics was less than 0.20 in ~600–10^5 Hz region, which rapidly decreased to a minimum value of 0.03 by La^{3+}doping with χ = 0.05. Our measurement of the ceramics conductivities (σ) also indicated that the appropriate introduction of La^{3+} into $CaCu_3Ti_4O_{12}$ would distinctly result in its dielectric properties.

Keywords: C. Dielectric properties; $CaCu_3Ti_4O_{12}$; Sol–gel method; La^{3+}doping

1. Introduction

The family of $ACu_3Ti_4O_{12}$ compounds has been intensively studied since 1967 [1]. In particular, the ceramic $CaCu_3Ti_4O_{12}$ (CCTO), due to its relatively high-dielectric constant (~10^4) and low-loss tangent (~10^{-1}) in a broad frequency range, is gaining increasing scientific attention for its potential applications in microelectronic devices [1–6]. Meanwhile, the family of $A_{2/3}Cu_3Ti_4O_{12}$, where A is a trivalent rare-earth ion, which has a similar structure of CCTO, has been reported frequently as well as the effect of chemical composition on the dielectric properties [1].

In recent years, it has been discovered that the dielectric constant of $La_{2/3}Cu_3Ti_4O_{12}$ ceramic is ~418 at 100 kHz at room temperature [1], which is much lower than that of $CaCu_3Ti_4O_{12}$ (~10^4). On the other hand, the high dielectric constant of the classic ceramic $BaTiO_3$ at room temperature could be significantly enhanced up to >25,000 by La-dopant, with appropriate compositions, temperatures and a novel doping mechanism [7]. Although the CCTO and $BaTiO_3$ ceramics have similar structures and high-dielectric constant, they have distinct mechanisms for the dielectric properties, which make it both necessary and interesting to investigate CCTO ceramic by doping of La^{3+}. Furthermore, it is known that the radius of the substituting element is an important parameter to determine the incorporation site [8]. The radius of ions as La^{3+} (1.15 Å) and Ca^{2+} (1.05 Å) are so close in value, which is another reason why we prefer La^{3+} to other ions as substituting Ca^{2+}.

In this paper, we managed to partially substitute Ca^{2+} with La^{3+} in CCTO for the first time. The different proportion of La^{3+} from $La(NO_3)_3{\cdot}6H_2O$ was introduced into CCTO to synthesize $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ (χ = 0.00, 0.05, 0.10, 0.15 and 0.20) ceramics through a sol–gel method and citrate auto-ignition way. The advantages of sol–gel method lie in the fact that the powders are characterized by nanometer sizes, a low sintering temperature and extraordinary mechanical properties [9]. The effects of La^{3+} doping on the dielectric properties of CCTO ceramic were studied.

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2. Experimental procedure

According to the composition of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ (χ = 0.00, 0.05, 0.10, 0.15 and 0.20), the stoichiometric amount of analytical grade $Ca(NO_3)_2\cdot 4H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $La(NO_3)_3\cdot 6H_2O$, $Ti(OC_4H_9)_4$ and citric acid were used as the raw materials. At first, $Ti(OC_4H_9)_4$ was dissolved into C_2H_5OH quickly with vigorous stirring, and then certain CH_3COOH was added into it immediately. About 10 min later, the nitric acid and deionized water were dropped in slowly. Then this solution was carefully mixed with another solution where appropriate nitrates had been dissolved in C_2H_5OH to form a new mixture. Finally, appropriate amount of citric acid was added into this mixture to get some transparent sol. The sol was slowly evaporated and dried to yield a blue xerogel, which was later annealed at 450 °C in an electrical muffle's furnace for ~75 min to become a loose and brown ash powder.

Hereafter the following procedure, the powders were ground and pressed at a pressure of 20 MPa into pellets with a diameter of 10 mm and a thickness of ~2 mm. The brown pellets were sintered in static air at 1000 °C for 2 h and the ceramic samples were obtained.

The differential thermal analysis (DTA) on the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ gels with 20 mg was performed between 20 and 720 °C in flowing dry air with an increase rate of 20 °C/min, by using a CRY-2 thermal analyzer. The crystalline phases of the sintered ceramics were identified by means of X-ray powder diffraction (XRD) using a Cu Kα radiation at the wavelength of 0.15406 nm in a range of 35–75°. The microstructures of the samples were observed using a scanning electron microscope (SEM). The dielectric constant (ε), loss tangent (tan δ) and conductivity (σ) of the ceramics coated with silver electrodes were obtained with a precision impedance analyzer over the frequency of 40–10^7 Hz at room temperature (300 K). Adopting the Archimedes method, we found the relative density of the resultant specimen $CaCu_3Ti_4O_{12}$ to reach up to ~90% after being heated at 1000 °C. In such cases, it may not be the high-density of ceramics but the processing of fabrication of the ceramics that really counts.

3. Results and discussion

Fig. 1 illustrates the DTA curves of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ (χ = 0.00, 0.05, 0.10, 0.15 and 0.20) gels heated in air in the temperature from 20 to 720 °C. The main endothermic peaks appeared at ~120 °C for all the five samples due to the evaporation of the absorbed water and C_2H_5OH. The main exothermic peaks were at ~380 °C, which was possibly attributed to the combustion of some organic contents. As shown in Fig. 1, the two kinds of peaks in the DTA curves shifted towards the lower temperature as χ values were increased. These results indicated that slight decrease of temperature of endothermic peaks and exothermic peaks occurred with the doping of La^{3+}. Almost no new peaks in the curves have been observed after 420 °C. Therefore, 450 °C was considered as an appropriate annealing temperature for the gels.

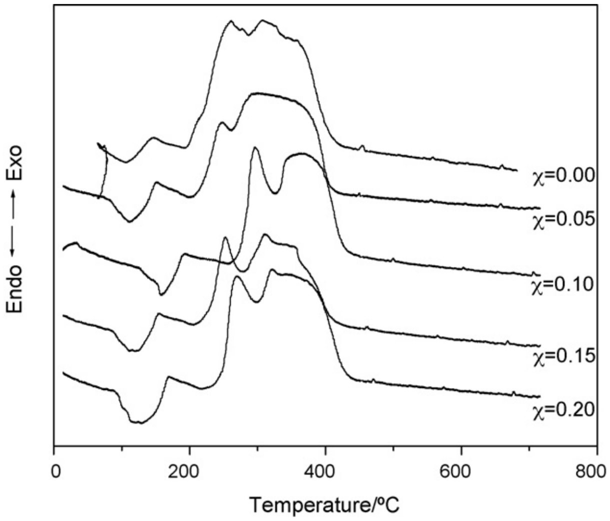

Fig. 1. DTA curves of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ (χ = 0.00, 0.05, 0.10, 0.15 and 0.20) gels.

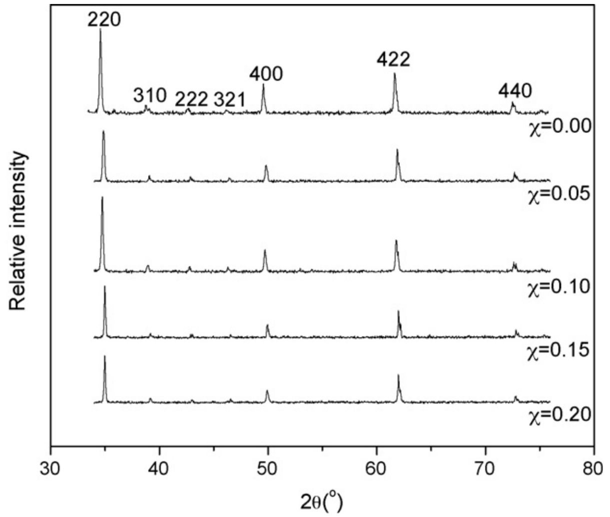

Fig. 2. XRD curves of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics (χ = 0.00, 0.05, 0.10, 0.15 and 0.20) sintered at 1000 °C for 2 h.

Fig. 2 illustrates the XRD patterns of the sintered $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ (χ = 0.00, 0.05, 0.10, 0.15 and 0.20) ceramics. The XRD patterns of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics were very similar with each other. Hassini et al. [6] and many others regarded the space group of CCTO as Im3 (no. 204), and the XRD patterns corresponding to this structure could be seen in all traces shown in the curve of sample with χ = 0.00. Thus it could be asserted that the reaction had reached almost complete at 1000 °C. The curves of samples with χ = 0.05–0.20 were almost identical with that of sample at χ = 0.00, and no independence of $La(NO_3)_3$ phases has been observed for samples with χ = 0.05–0.20, which indicated that La^{3+} did almost not influence the crystalline structure. According to Fig. 2, increasing the χ value, the lattice peaks of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ system linearly decreased. The XRD patterns also presented that the average grain size of samples at χ = 0.00–0.20 was ~1–2 μm estimated by Scherrer's equation [9].

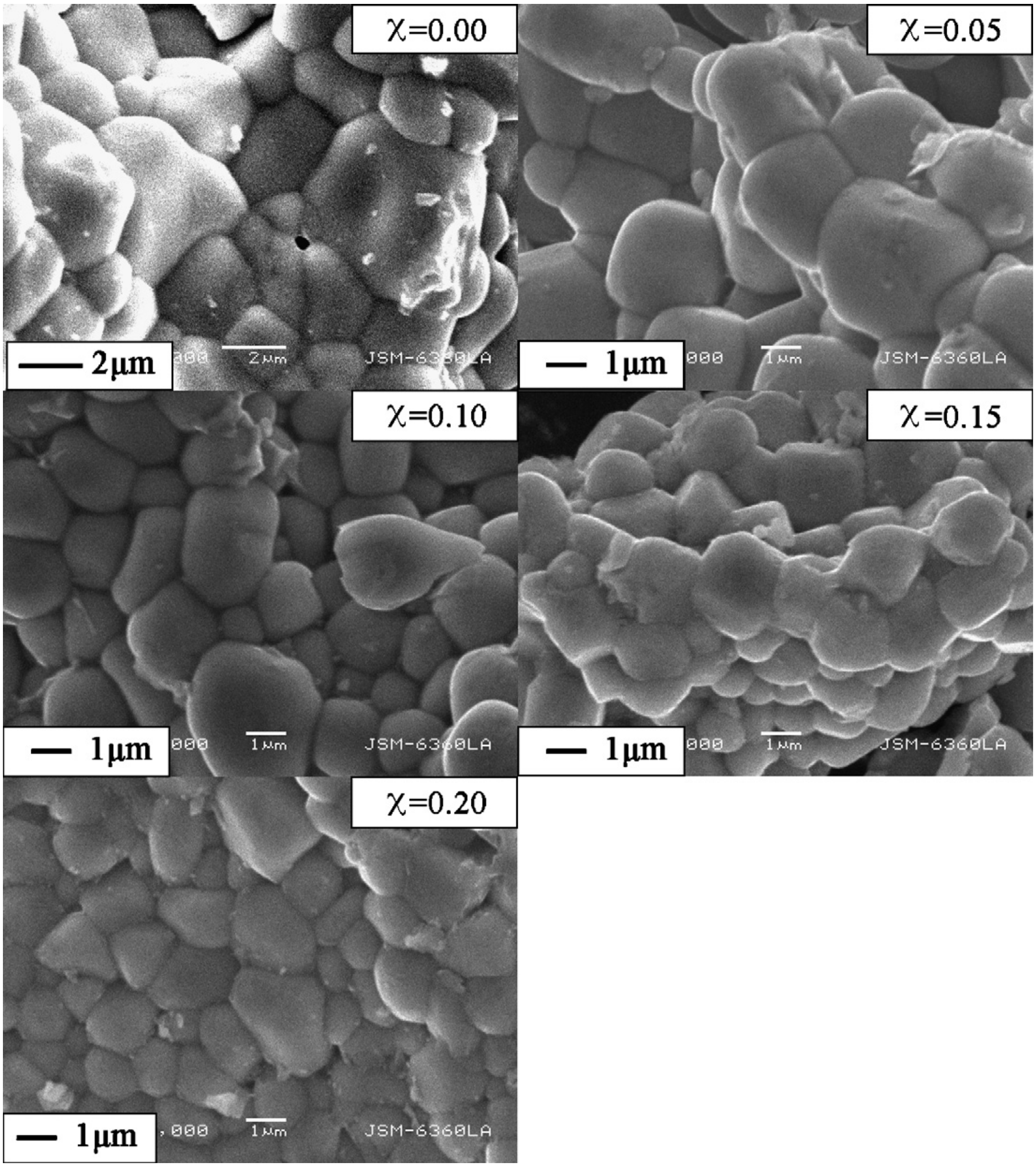

Fig. 3. The SEM images of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics ($\chi = 0.00$, 0.05, 0.10, 0.15 and 0.20) sintered at 1000 °C for 2 h.

Fig. 3 demonstrates the SEM images of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics with different χ values sintered at 1000 °C for 2 h. It can be seen that the specimens displayed a homogeneous microstructure with an average grain size of about ~1–2 μm, which consisted well with the results we calculated from Fig. 2. The average grain size of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics remained almost the same despite the variation of χ values. The sizes of these particles made from powders synthesized via sol–gel route were relatively smaller than those from the ceramic method reported in Ref. [5]. Therefore, it could be affirmed that the sol–gel method is an effective way to synthesize powders of nanometer sizes. As could be seen from Fig. 3, the grains assembled very compactly, which may affect the dielectric properties of the ceramics [5].

Fig. 4 illustrates the variation of dielectric constant (ε) of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics sintered at 1000 °C for 2 h for various χ values. Here, ε showed a constant value of the order of

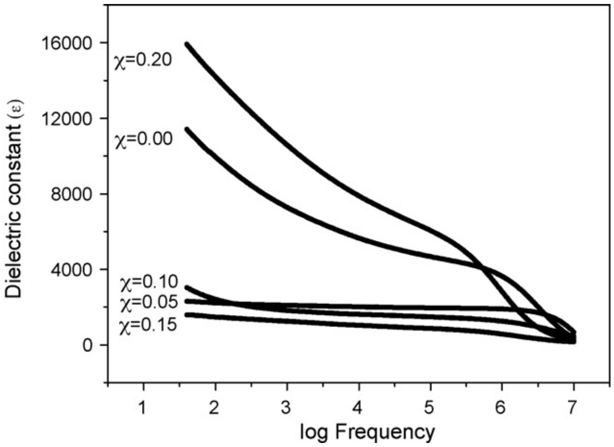

Fig. 4. Comparison of the dielectric constant (ε) of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics ($\chi = 0.00$, 0.05, 0.10, 0.15 and 0.20) sintered at 1000 °C for 2 h.

$\sim 10^3$–10^4 for all the samples at the frequencies of 10^2–10^6 Hz, and then decreased sharply when the frequency got higher than 10^6 Hz. The large values of ε under ∼100 Hz may be associated with the problem of electrode contact. And the drastic decrease in ε at high frequencies, $>10^6$ Hz, may indicate the presence of conductive grains [10]. Morrison et al. [7] had suggested an alternative mechanism, namely, oxygen loss according to "$O^{2-} \rightarrow V_O + 1/2O_2 + 2e^-$" was responsible for the conductivity.

As could be seen from Fig. 4, the ε values of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ samples with $\chi = 0.05$–0.20 were a little smaller than the value of sample with $\chi = 0.00$. The ε_{max} values became gradually smaller as the χ value increased from 0.05 to 0.15. However, as χ increased up to 0.20, the ε_{max} value became considerably high, which was almost higher than that of sample with $\chi = 0.00$. Cation distortions may exist and be attributed to this phenomenon [10]. In addition, the curves about ε values of samples with $\chi = 0.05$–0.15 were fairly flat while the curves of $\chi = 0.20$ and $\chi = 0.00$ were much steeper. Consequently, appropriately substituting Ca^{2+} with La^{3+} in CCTO can greatly enhance the dielectric properties of the ceramics. And for χ from 0.05 to 0.15, ε values became smaller with the increasing concentration of La^{3+}. Each ε value of samples with $\chi = 0.05$–0.15 taken from the intermediate-frequency ranging from 10^2 to 10^6 Hz showed little variation. However, in the case of La^{3+}-doped $BaTiO_3$, the dielectric constant of the new ceramic varied greatly with the doping of La^{3+} at different frequencies [7]. From the above discussion, a conclusion could be drawn that comparing with CCTO, the La^{3+} doping into CCTO resulted in a flat dielectric constant curve, and the ε value reduced to a certain degree. It was indicated that the mechanism of La^{3+} doping into CCTO was quite different from that of the ions into $BaTiO_3$, although the differences were not illuminated at present.

Fig. 5 illustrates the loss tangent (tan δ) values of the $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics with different concentrations of La^{3+} at room temperature at different frequencies. It is observed that the curves passed through a minimum tan δ value of 0.15, 0.03, 0.06, 0.15 and 0.20 at ∼50 kHz, respectively. The general behavior of tan δ curves was very similar although the tan δ values differed significantly. Over the frequency range from 10^2 to 10^5 Hz, tan δ values at $\chi = 0.05$–0.20 were small and almost not varied with frequency and the tan δ values were less than 0.20 in ∼600–10^5 Hz region. However, the tan δ value at $\chi = 0.00$ varied strongly with the increase of frequency. For samples with $\chi = 0.05$–0.15, the tan δ values became higher as the concentration of La^{3+} grew up. The reversed tendency of ε variation of samples with $\chi = 0.05$–0.15 as shown in Fig. 4 and these tan δ behavior may have potential applications. As could be seen in Fig. 5, sample with $\chi = 0.05$ possessed the lowest tan δ value and sample with $\chi = 0.00$ showed much higher tan δ value. The curves of $\chi = 0.05$–0.20 were relatively flat, and which were similar to the ε curves shown in Fig. 4 to some extent. Therefore, the proportional introduction of La^{3+} can not only flat the dielectric-value curves of the ceramics but also greatly reduce the tan δ values of the ceramics.

The analysis of conductivity σ was an effective method to investigate the properties and microstructure of the ceramics, which reflected the difference of the interior and boundary of the ceramics. Fig. 6 illustrates the dependence of σ in the frequency from 40 to100 kHz at room temperature. σ, the conductivity of the ceramics, can be derived from the equation $\sigma = L/SR$, where L and S were the thickness and bottom area of the pellet, respectively. Impedance R can be measured by a precision impedance analyzer. From Fig. 6, we can get that the σ values of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics did not show any regulation with χ values. The σ value increased drastically with the increasing frequency in the region of the whole frequencies. There was a tendency of σ to increase with the increase of frequency when it was higher than 100 kHz. This result was in good agreement with that in Zhao et al. [11]. A reasonable conclusion drawn by Zhao was that the different behavior of σ depending on frequencies in the range of low frequencies and high frequencies was due to interfacial effect [11]. In addition, Pollak and Geballe considered that the behavior of σ could be explained in terms of hopping mechanism at high frequencies, but the hopping dispersion was

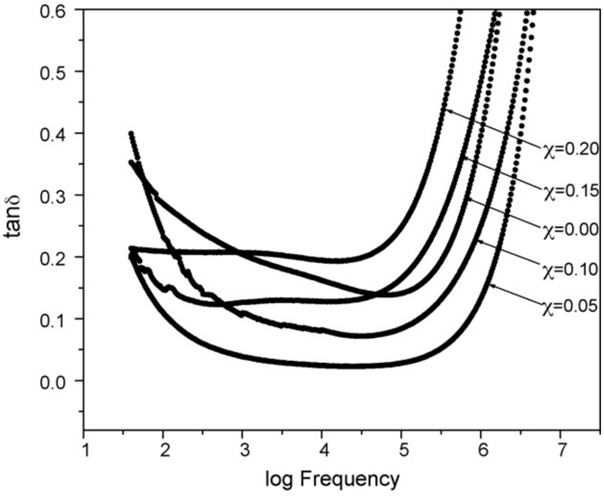

Fig. 5. Comparison of loss tangent (tan δ) of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics ($\chi = 0.00$, 0.05, 0.10, 0.15 and 0.20) sintered at 1000 °C for 2 h.

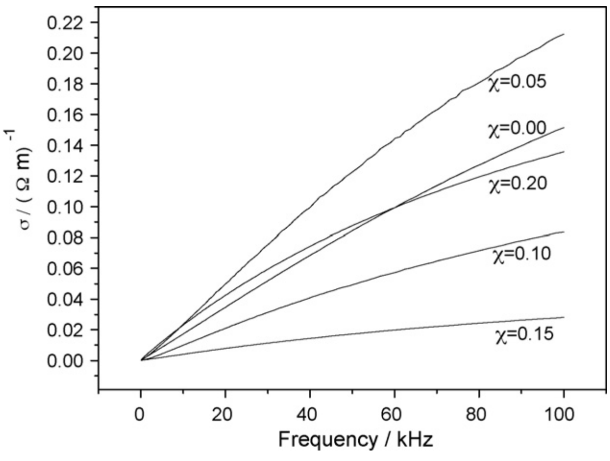

Fig. 6. Comparison of the conductivity (σ) of $Ca_{1-\chi}La_{2\chi/3}Cu_3Ti_4O_{12}$ ceramics ($\chi = 0.00$, 0.05, 0.10, 0.15 and 0.20) sintered at 1000 °C for 2 h.

influenced by an additional polarization mechanism at low frequencies [12].

4. Conclusions

We found that the appropriate introduction of La^{3+} into CCTO could greatly flat the ε value curves at the frequency ranging from 10^2 to 10^6 Hz with some decrease of the dielectric constant. The low and almost none frequency dependant tangent values decreased from 0.20 to 0.03 for samples with $\chi = 0.20$–0.05, respectively, which was superior to that of CCTO ceramic too. Our investigations suggested that the flat ε value and smaller tangent value should be owing to the concentration of La^{3+} ion in ceramics.

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