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Ceramics International 39 (2013) S149–S152

CERAMICS INTERNATIONAL

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Dielectric properties of Sm-doped $CaCu_3Ti_4O_{12}$ ceramics

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Available online 17 October 2012

Abstract

The effects of Sm substitution on structure, dielectric properties and conductivity of $CaCu_3Ti_4O_{12}$ ceramics were investigated. $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ (x = 0.0%, 0.5%, 1.0%) ceramics were synthesized by the solid-state reaction method. Single phase crystal of the ceramics with space group *Im*3 was obtained. With increasing Sm content, the dielectric loss of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics improved but the dielectric constant also decreased significantly, with both the low- and high-temperature dielectric relaxations suppressed.

Keywords: B. Defects; C. Dielectric properties; $CaCu_3Ti_4O_{12}$ ceramics

1. Introduction

In recent years, perovskite-like $CaCu_3Ti_4O_{12}$ has attracted considerable scientific attention due to its giant, static dielectric constant (of the order 10^4–10^5) in a broad temperature range from 100 to 400 K, which promotes the potential application of this material in the fields of microelectronics and memory devices, such as static and dynamic random access memories [1–5]. In order to explain the giant dielectric constant, several models about extrinsic and intrinsic origins have been proposed [6,7], while the effects of the oxygen vacancy and the mixed-valence structure correlated with the oxygen vacancies should be considered [8,9].

On the other hand, although $CaCu_3Ti_4O_{12}$ possesses giant dielectric constant, the dielectric loss is too high for commercialization. So numerous efforts have been made to suppress the dielectric loss but maintaining high dielectric constant by various compositional modifications such as substitution of Mn, La, Zn for Cu [10,11,5], La for Ca [12], and Zr, Al, Nb for Ti [13–15].

In the present investigation, Ca^{2+} is partially substituted by Sm^{3+} ion according to the nominal formula of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ (x = 0.0%, 0.5%, 1.0%) under optimum sintering conditions. The effects of Sm substitution on the microstructure and dielectric properties are investigated.

2. Materials and methods

2.1. Preparation of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics

The objective ceramics of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ (x = 0.0%, 0.5%, 1.0%) were prepared via the conventional solid state reaction method. Appropriate amounts of Reagent-grade $CaCO_3$ (99%), CuO(99%), TiO_2 (99.5%) and Nd_2O_3 (99.9%) were weighed and mixed in a ball mill using zirconia as grinding media and ethanol as a mixing medium for 24 h. The powders were dried and calcined at 1123 K for 3 h in air, and then pressed into green pellets (16 mm in diameter and 2–3 mm in thickness) with 5 wt% polyvinyl alcohol solution as a binder under a uniaxial pressure of 98 MPa. The pellets were slowly heated to 823 K and held at this temperature for an hour to burn off the binder, and then sintered at 1000–1100 °C in air for 3 h with the heating rate of 5 °C per minute to yield the dense ceramics. The obtained samples were cooled inside a furnace naturally.

2.2. Characterization

X-ray powder diffraction (XRD) was performed on an ARLX′TRA diffractometer (Thermo Electron) with Cu Kα radiation (λ = 0.15405 nm). The dielectric characteristics of the ceramic samples which were electroded by silver paint

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http://dx.doi.org/10.1016/j.ceramint.2012.10.052

fired at 600 °C for 30 min were evaluated with a broadband dielectric spectrometer (Turkey Concept 50, Novocontrol Technologies) in a broad range of temperature (150–550 K) and frequency (1 Hz to 10 MHz).

3. Results and discussion

All the $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ($x=0.0\%$, 0.5%, 1.0%) ceramics were well sintered at 1050 °C for 3 h. X-ray diffraction patterns of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics are shown in Fig. 1. All the diffraction peaks were identified to a body-centered cubic structure with space group *Im*3 in agreement with JCPDs file No. 21-0140, and no secondary phase.

Fig. 2 shows the frequency dependence of the dielectric properties for $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ($x=0.0\%$, 0.5%, 1.0%) ceramics at 300 K. As shown in Fig. 2(a), the dielectric constant has a plateau, indicating the frequency-independence over the frequency range 10–10^5 Hz, and a sharp decline around 10^5 Hz. With increasing Sm content, the magnitude of the dielectric constant at the frequency of 10 kHz decreases significantly from $\varepsilon'=20{,}276$ for undoped $CaCu_3Ti_4O_{12}$ ceramics to $\varepsilon'=8101$ for $x=0.5\%$ and $\varepsilon'=925$ for $x=1.0\%$. There are two obvious Debye-like relaxations at low and high frequencies, which can also be observed in the dielectric loss tangent plot shown in Fig. 2(b). Substitution of Sm for Ca improves the dielectric loss of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics, and tan δ decreases from 0.093 for the undoped $CaCu_3Ti_4O_{12}$ ceramics to 0.065 for $x=0.5\%$ and 0.77 for $x=1.0\%$.

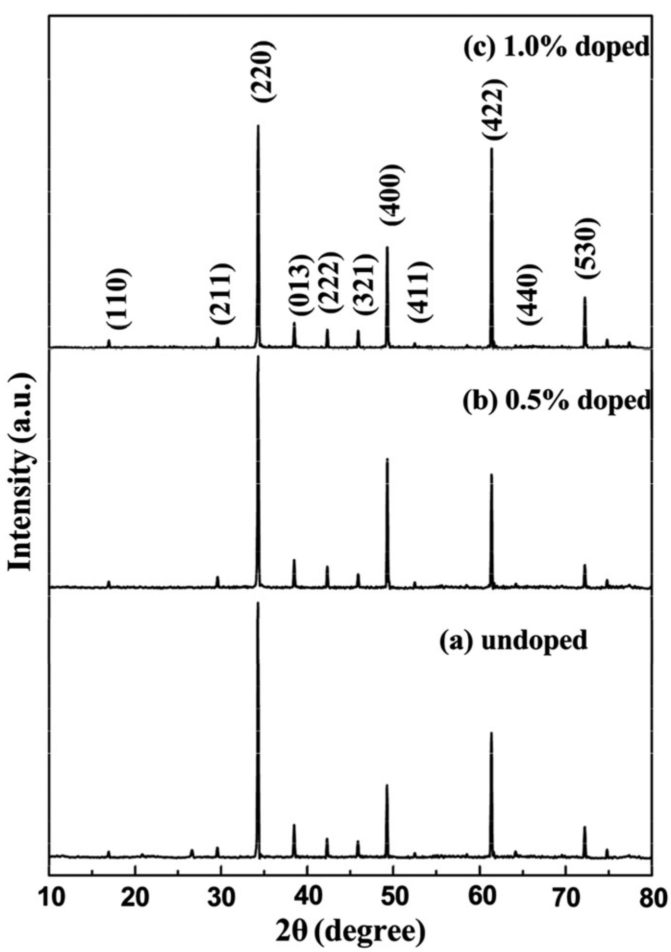

Fig. 1. X-ray diffraction patterns of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics sintered at 1050 °C for 3 h: (a) $x=0.0\%$, (b) $x=0.1\%$, (c) $x=0.5\%$, and (d) $x=1.0\%$.

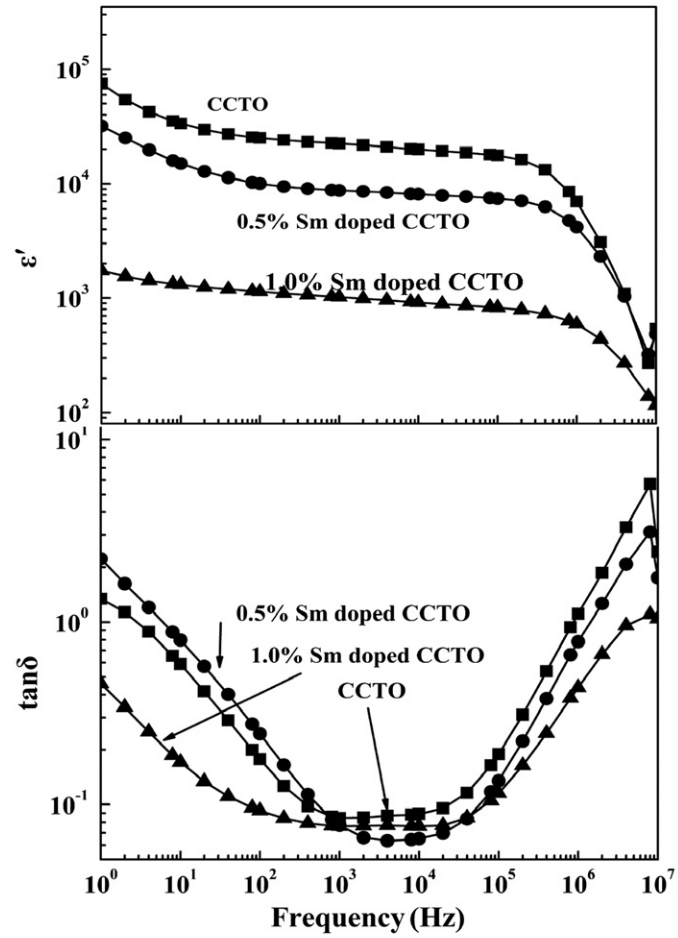

Fig. 2. Frequency dependences of (a) dielectric constant and (b) dielectric loss of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics sintered at 1050 °C for 3 h.

Temperature dependences of dielectric constant and dielectric loss for $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ($x=0.0\%$, 0.5%, 1.0%) ceramics sintered at 1050 °C for 3 h are shown in Fig. 3. There are two obvious dielectric relaxations at low and high temperatures and a giant dielectric constant plateau. With increasing Sm content, the low- and high-temperature dielectric relaxations are suppressed and the magnitude of the dielectric constant plateau is lowered. In order to declare the effect of Sm substitution on dielectric response, the change of two dielectric relaxations is investigated.

To understand the physical nature of the dielectric abnormities of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ($x=0.0\%$, 0.5%, 1.0%) ceramics mentioned above, the frequency dependence of the dielectric constant is plotted for a lower temperature range, and these data are fitted with the modified Debye equation [16,17]

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1+(i\omega\tau)^{1-\alpha}], \quad (1)$$

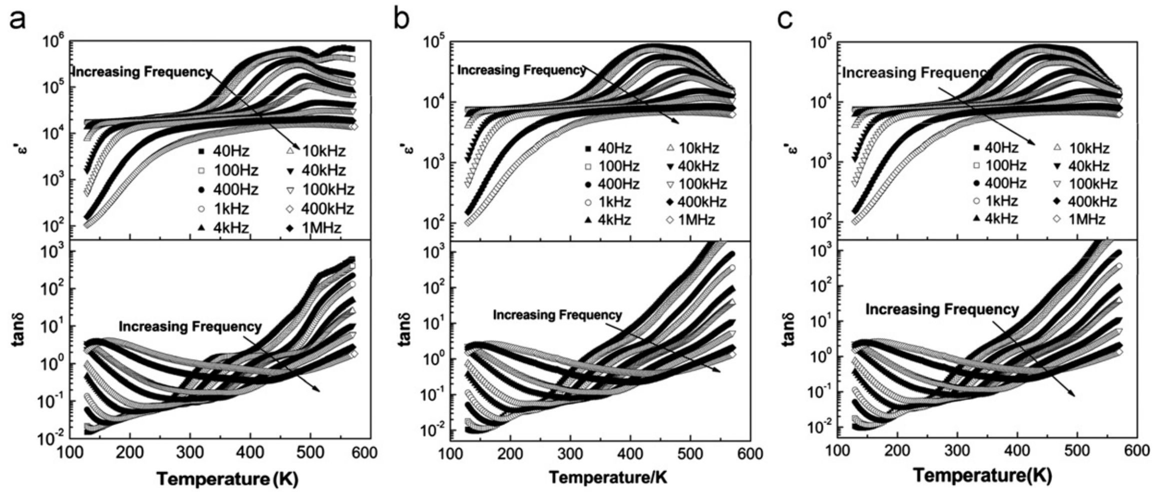

Fig. 3. Temperature dependences of dielectric constant and loss of $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics sintered at 1050 °C for 3 h: (a) $x=0\%$, (b) $x=0.5\%$, and (c) $x=1.0\%$.

where ω is the angular frequency, τ is the mean relaxation time, α is a measure of the distribution of relaxation time, ε_0 is the static dielectric constant, and ε_∞ is the dielectric constant at light frequencies. The variation of τ with $1/T$ is fitted with the Arrhenius law

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (2)$$

where τ_0 is the pre-exponential term, E_a is the activation energy and k_B is the Boltzmann parameter. As shown in Fig. 4, a nearly monodispersive nature of the dielectric relaxation is indicated in the present ceramics at lower temperatures with a very small α parameter (0.0530–0.1031). The activation energy is 87 meV for $x=0\%$, 94 meV for $x=0.5\%$, and 68 meV for $x=1.0\%$, which is close to that of hopping of charge carriers between Cu^+/Cu^{2+} and Ti^{3+}/Ti^{4+}, indicating that the low temperature relaxation may be related to the hopping of charge carriers between Cu^+/Cu^{2+} and Ti^{3+}/Ti^{4+} mixed-valence structures. The activation energy increased when 0.5% Sm was doped for Ca, which can be considered as the result of decrease of Cu^+/Cu^{2+} and Ti^{3+}/Ti^{4+} mixed-valent structures. With further increasing Sm content, the pre-exponential relaxation time, which is related to the thermal vibration of ions which is the feature for dielectric itself, increases significantly although the activation energy decreases.

The high temperature relaxation of $CaCu_3Ti_4O_{12}$ has been reported to be closely related to the high temperature conductivity according to the almost same activated temperature. So the dc conductivity in the high temperature region is fitted by the Arrhenius law

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right), \quad (3)$$

where σ_0 is the pre-exponential term which is a temperature independent constant, E_a is the activation energy for conductivity and k_B is the Boltzmann parameter. As shown

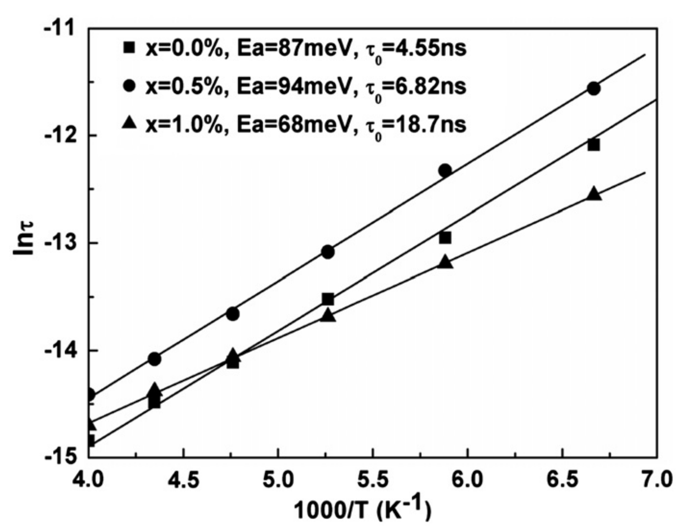

Fig. 4. Temperature dependence of relaxation time for $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$. Solid symbols are experimental data, and the lines are fitting curves according to the Arrhenius law.

in Fig. 5, it is found that the temperature dependence of the dc conductivity can be well fitted with Eq. (3). The conductivity activation energy is 0.77 eV for $x=0\%$, 0.68 eV for $x=0.5\%$, and 0.77 eV for $x=1.0\%$, and is not far from 0.7 eV which is the conduction activated energy of the electrons from second ionization of oxygen vacancies.

The results show slight increase of conductivity activation energy with increasing Sm substitution.

4. Conclusion

In conclusion, $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ($x=0.0\%$, 0.5%, 1.0%) ceramics with a cubic structure in space group *Im3* are prepared by the solid-state reaction method. The giant dielectric constant step is suppressed with

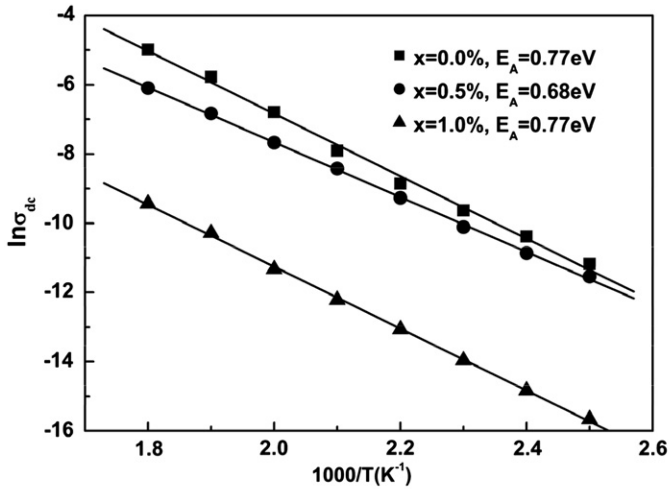

Fig. 5. Temperature dependence of dc conductivity for $Ca_{1-x}Sm_xCu_3Ti_4O_{12}$ ceramics. Solid symbols are experimental data, and the lines are fitting curves according to the Arrhenius law.

Sm-substitution by weakening both the low and high dielectric relaxations. The room temperature dielectric constant and dielectric loss decrease with increasing Sm substitution.

Acknowledgments

The present work was supported by Qianjiang Project of Zhejiang Province under Grant no. 2009R10038.

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