

# High dielectric constant in $(1-x)\text{SrTiO}_3/x\text{CuO}$ composite ceramics

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**Abstract** Semiconductive secondary phase CuO was introduced into  $\text{SrTiO}_3$  ceramic matrix to yield dielectric composite ceramics with high dielectric constant. The dense composite ceramics could be obtained by sintering at  $1050^\circ\text{C}$  in air for 3 h, in which the co-presence of  $\text{SrTiO}_3$  and  $\text{CuO}/\text{Cu}_2\text{O}$  was confirmed. The dielectric constant of the present composite ceramics increased firstly and then decreased with increasing the content of CuO, and the highest dielectric constant was obtained at  $x=0.4$ . There were steps and peaks on the curves of dielectric constant vs temperature and dielectric loss vs temperature, respectively, and the peak temperatures of dielectric loss indicated the Debye-type relaxation.

**Keywords**  $(1-x)\text{SrTiO}_3/x\text{CuO}$  · Composites · Dielectric properties · Microstructure

## 1 Introduction

High dielectric constant materials have numerous important applications in electronic devices such as capacitors, static and dynamical random access memories, and so on. So far, the commonly used high dielectric constant materials are ferroelectrics and relaxor ferroelectrics, in which a sharp or a diffused Curie peak is indicated on the curve of dielectric constant vs temperature. Usually, this significant temperature dependence of dielectric constant is undesirable for most applications. Recently, a new perovskite-related

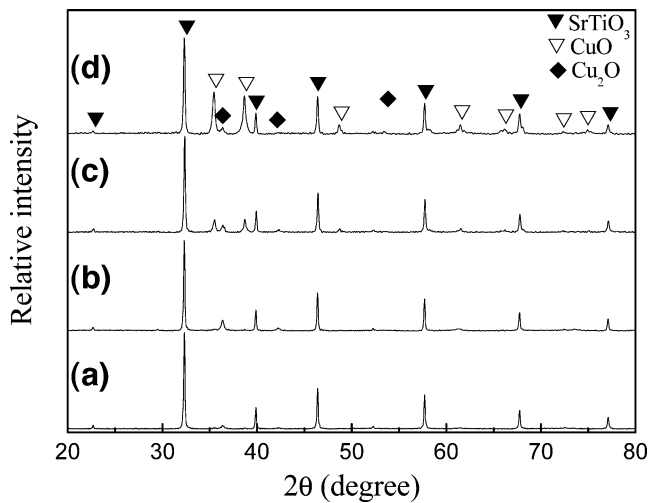
material,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , which has nearly temperature-independent giant dielectric constant about 10,000 over the wide temperature range of 100–500 K, in both the ceramic and single crystal forms, has been reported [1, 2]. Such characteristics are of great interest for practice and several mechanisms have been already proposed [3, 4]. There are two other groups of monolithic phase ceramics with giant dielectric constant,  $\text{AFe}_{1/2}\text{B}_{1/2}\text{O}_3$  ( $\text{A}=\text{Ba}, \text{Sr}; \text{B}=\text{Nb}, \text{Ta}$ ) [5, 6] and Li-doped NiO [7, 8]. While for composite ceramics, Pecharroman et al. [9] have introduced metal particle Ni into  $\text{BaTiO}_3$  ceramic matrix, the highest dielectric constant of 80,000 has been obtained, and the theory of percolation has been used to explain the origin of high dielectric constant. In the metal particle dispersed composite ceramics, metal particles are easy to be oxidized, which will make the sintering process more complicated as a protective atmosphere is required.

In the present work, the semiconducting CuO oxide has been introduced to the  $\text{SrTiO}_3$  ceramic matrix to overcome the problems induced by the oxidation of metal secondary phase, and the dielectric characteristics are evaluated together with their microstructure.

## 2 Experimental

Reagent-grade  $\text{SrCO}_3$  (99.95%),  $\text{TiO}_2$  (99.5%) in a 1:1 molar ratio were mixed by ball milling in deionized water using zirconia balls for 24 h. The slurry was dried and then calcined at  $1200^\circ\text{C}$  in air for 3 h to prepare  $\text{SrTiO}_3$  powders. Then the as-received CuO (99%) powders and  $\text{SrTiO}_3$  powders were mixed in the formula of  $(1-x)\text{SrTiO}_3/x\text{CuO}$  ( $x=0.2, 0.4, 0.6, 0.8$ , in mol.%) by ball milling using zirconia media in deionized water for 24 h. After drying, such mixed powders were pressed into disc

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**Fig. 1** XRD patterns of  $(1-x)\text{SrTiO}_3/x\text{CuO}$  composite ceramics: (a)  $x=0.2$ , (b)  $x=0.4$ , (c)  $x=0.6$  and (d)  $x=0.8$

compacts of 12 mm in diameter and 1 to 4 mm in height, and these compacts were sintered at 1050°C in air for 3 h to yield the dense ceramics.

The microstructures were evaluated by scanning electron microscope (SEM, JEOL JSM-5610LV), and the phase

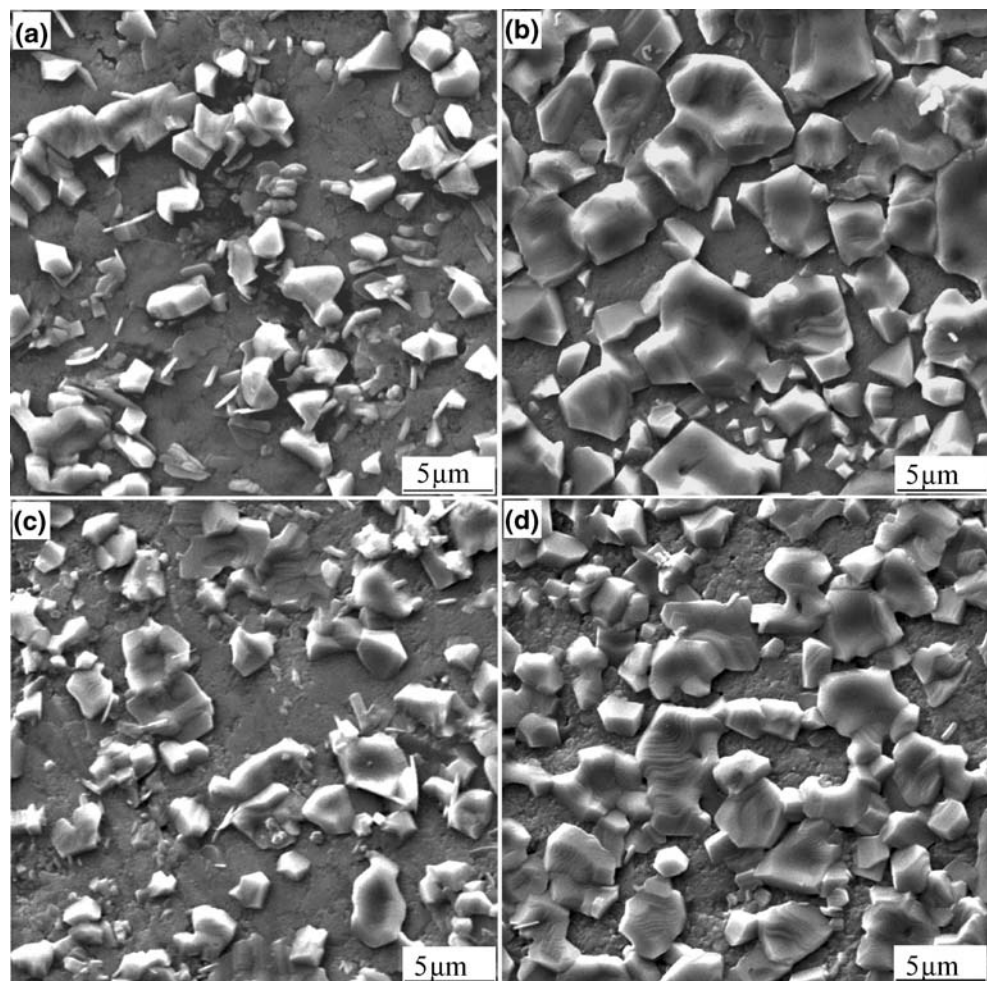
constitution of the present ceramics was characterized by X-ray diffraction (XRD, RIGAKU D/max 2550 PC) analysis using  $\text{CuK}\alpha$  radiation for crushed and ground powders.

The dielectric properties of the present ceramics at varied frequencies were measured by a precise LCR meter (HP 4284A), and the temperature coefficient of dielectric constant was evaluated at temperature ranging from 30 to 600°C.

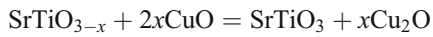
### 3 Results and discussion

XRD patterns of  $(1-x)\text{SrTiO}_3/x\text{CuO}$  dense ceramics are shown in Fig. 1, the composite ceramics consist of  $\text{SrTiO}_3$ ,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  phases, and the secondary phase is almost  $\text{Cu}_2\text{O}$  when  $x \leq 0.4$ , and the ratio of  $\text{Cu}_2\text{O}$  phase decreases with increasing  $x$ . It is known that  $\text{CuO}$  changes to  $\text{Cu}_2\text{O}$  at about 1100°C, while the electrical conductivity changes from  $10^{-5} \text{ S cm}^{-1}(\text{CuO})$  to  $10^{-3} \text{ S cm}^{-1}(\text{Cu}_2\text{O})$  [10]. In the present work,  $\text{Cu}_2\text{O}$  secondary phase is detected in the samples sintered at 1050°C. Actually,  $\text{CuO}$  was surrounded

**Fig. 2** SEM micrographs of  $(1-x)\text{SrTiO}_3/x\text{CuO}$  composite ceramics: (a)  $x=0.2$ , (b)  $x=0.4$ , (c)  $x=0.6$  and (d)  $x=0.8$

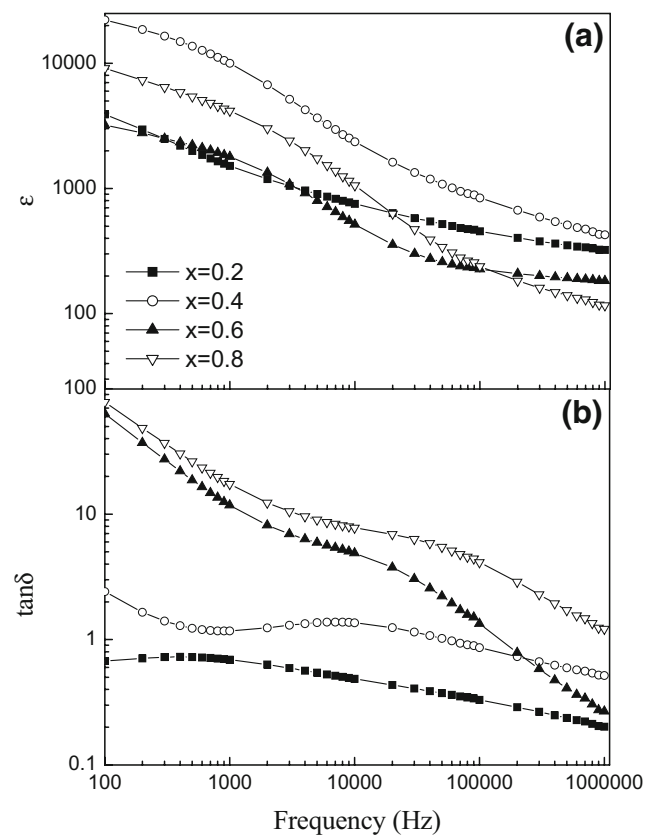


by SrTiO<sub>3</sub> matrix, which will provide a reductive atmosphere during sintering. The reaction

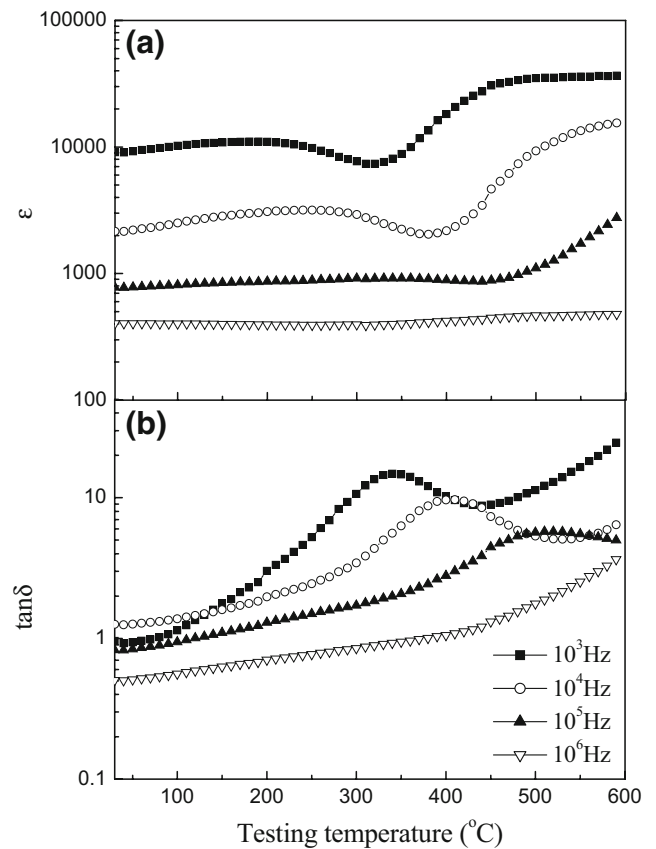


might occur during the sintering process which leads to the decrease of the transition temperature of CuO to Cu<sub>2</sub>O. However, the reductive atmosphere is greatly weakened by increasing the content of CuO and reducing the SrTiO<sub>3</sub> reductive matrix. This is why we get different copper oxide secondary phases under the same sintering condition for the different compositions. The microstructures of composite ceramics are shown in Fig. 2. The grain size of CuO or Cu<sub>2</sub>O phase is several microns, while that of SrTiO<sub>3</sub> ceramic matrix is very small, and this should be due to the sintering temperature is high enough for the grain growth of CuO/Cu<sub>2</sub>O but is too low for the grain growth of SrTiO<sub>3</sub>.

The dielectric constant and dielectric loss of (1-x)SrTiO<sub>3</sub>/xCuO composite ceramics decrease with increasing frequency (see Fig. 3), while the scope of variations increases with the contents of CuO additive. The dielectric constant increases firstly and then decreases with the increasing content of CuO additive, the highest value has been obtained at x=0.4 where almost CuO changes into Cu<sub>2</sub>O and the largest content of Cu<sub>2</sub>O secondary phase is

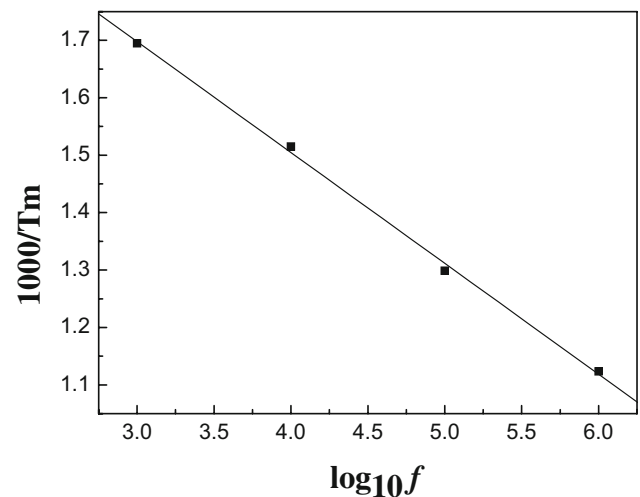


**Fig. 3** Frequency dependence of (a) dielectric constant and (b) dielectric loss of (1-x)SrTiO<sub>3</sub>/xCuO composite ceramics



**Fig. 4** Temperature dependence of (a) dielectric constant and (b) dielectric loss of 0.6SrTiO<sub>3</sub>/0.4CuO composite ceramics

detected. When a conductive phase has been introduced into the insulating matrix to constitute a heterogeneous media that subjected to an ac field, the charge carriers in the conductive grains can move within the particles, but can not move outside the boundaries of these particles, hence they accumulate at the interfaces. This phenomenon is called interfacial polarization, or Maxwell–Wagner polarization



**Fig. 5** Plot of 1000/*T<sub>m</sub>* vs log<sub>10</sub>*f*, where *T<sub>m</sub>* is the temperature of the loss peak under certain measure frequency

[11]. If the difference of electrical conductivities of two phases is large, the dielectric constant contributed from interfacial polarization is high. In the present composite ceramics, the relatively conductive phase  $\text{Cu}_2\text{O}$  or  $\text{CuO}$  is observed in the relative insulating matrix  $\text{SrTiO}_3$  and interfacial polarization is the main contribution for the high dielectric constant of the composite ceramics. As shown in Fig. 1, the primary secondary phase for  $x=0.4$  is  $\text{Cu}_2\text{O}$ , while that for  $x=0.6$  and  $0.8$  is  $\text{CuO}$ , so the highest dielectric constant obtained at  $x=0.4$  should be due to the higher electrical conductivity of  $\text{Cu}_2\text{O}$  phase. Also, the grain size of the secondary phase is the largest, and the region between two secondary phase grains is the narrowest for  $x=0.4$  (see Fig. 2). The dielectric constant of composite ceramics is in direct ratio with the ratio of the above two dimensions as predicted by Maxwell–Wagner theory, and this is another reason for the highest dielectric constant obtained in  $0.6\text{SrTiO}_3/0.4\text{CuO}$  composite ceramics.

The temperature dependence of dielectric constant and dielectric loss of  $0.6\text{SrTiO}_3/0.4\text{CuO}$  composite ceramics is shown in Fig. 4. The dielectric constant increases monotonically with temperature at 1 MHz, while there is a step for other frequencies, which is corresponding to the peak on the curve of dielectric loss, and the peak temperature increases with the increasing testing frequency. In Debye-type relaxation, relaxation time  $\tau$  varies with temperature  $T$ , typically  $\tau = \tau_0 \text{Exp}(E_a/k_B T)$ , where  $\tau_0$  is the prefactor,  $E_a$  the activation energy for the response, and  $k_B$  the Boltzmann constant. The fact that the plot of  $\log_{10} f$  vs  $1,000/T_m$  is linear (see Fig. 5) confirms that the relaxation in the present composite ceramics is the typical Debye-type relaxation [6], where  $f$  is frequency and  $T_m$  is the peak temperature of  $\tan\delta$ .

#### 4 Conclusion

Semiconductive copper oxide secondary phases could coexist with  $\text{SrTiO}_3$  ceramic matrix, the primary secondary

phase was  $\text{Cu}_2\text{O}$  when  $x \leq 0.4$ , and it changed to  $\text{CuO}$  when  $x > 0.4$ . The dielectric constant increased firstly to a maximum value and then decreased with increasing the content of  $\text{CuO}$  additive, and this could be explained by Maxwell–Wagner relaxation theory. There were steps and peaks on the curves of dielectric constant vs temperature and dielectric loss vs temperature, and the peak temperatures increased with increasing frequency, which was the typical Debye-type relaxation.

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