Dielectric and varistor properties of rare-earth-doped ZnO and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ composite ceramics

Huafei Lu, Yuanhua Lin*, Jiancong Yuan, Cewen Nan and Kexin Chen
*State Key Laboratory of New Ceramics and Fine Processing,
Department of Materials Science and Engineering,
Tsinghua University, Beijing 100084, P. R. China*
*linyh@tsinghua.edu.cn

Received 22 June 2012; Revised 14 November 2012; Accepted 15 January 2013; Published 21 February 2013

To investigate the multi-functional ceramics with both high permittivity and large nonlinear coefficient, we have prepared rare-earth Tb-and-Co doped ZnO and TiO_2 -rich $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (TCCTO) powders by chemical co-precipitation and sol-gel methods respectively, and then obtained the TCCTO/ZnO composite ceramics, sintered at 1100°C for 3 h in air. Analyzing the composite ceramics of the microstructure and phase composition indicated that the composite ceramics were composed of the main phases of ZnO and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO). Our results revealed that the TCCTO/ZnO composite ceramics showed both high dielectric and good nonlinear electrical behaviors. The composite ceramic of TCCTO: ZnO = 0.3 exhibited a high dielectric constant of ~ 210 (1 kHz) with a nonlinear coefficient of ~ 11 . The dielectric behavior of TCCTO/ZnO composite could be explained by the mixture rule. With the high dielectric permittivity and tunable varistor behaviors, the composite ceramics has a potential application for the higher voltage transportation devices.

Keywords: Varistors; CCTO; nonlinear coefficient; dielectrics.

1. Introduction

With the development of electronic technology, high-performance devices with multi-function, integration as well as miniaturization are highly desired. ZnO-based varistors^{1,2} have been widely used in electronic circuit, devices and electrical power systems to protect against overvoltage surges, due to their large nonlinear exponent and energy absorption capacity. Most commercial ZnO varistors are traditional ZnO ceramics^{3,4} with additives as Bi_2O_3 , Sb_2O_3 , MnO, Co_2O_3 and Cr_2O_3 , and it has been investigated that rare-earth oxides-doped ZnO varistors^{5,6} show significant nonlinearity. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)^{7–9} exhibits giant dielectric permittivity ($\epsilon \sim 104$), which possesses good temperature stability (100–400 K) and frequency stability (100 Hz–1 MHz). However, the nonlinear electrical behaviors of CCTO or doped-CCTO^{10–12} are always weak in contrast with ZnO.

Our previous work^{13,14} also revealed that the dielectric and the varistor properties of TCCTO could be tuned by the additional content of TiO_2 . Though CCTO (or TCCTO) exhibits high dielectric constant property, the varistor behavior is regularly weak. However, ZnO-based varistor shows large nonlinear characteristics, while the dielectric constant⁶ is regularly low. Considering their high dielectric and large nonlinear behavior, it is highly desirable to obtain a multi-functional composite ceramic of TCCTO and ZnO. So this kind of composite ceramics should have both high dielectric constant and nonlinear coefficient in one electric device, which has great potential in the high integrated circuits,

especially for the application in the ultrahigh-voltage transportation devices.

In this work, we prepared a composite ceramic of rare-earth-doped ZnO and TiO_2 -rich $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (TCCTO), and investigated the dielectric and nonlinear behaviors. The results revealed that the composite ceramics of TCCTO/ZnO can show both high dielectric and good nonlinear properties.

2. Experimental Procedure

The rare-earth-doped ZnO powders were prepared by a chemical co-precipitation method. Analytical grades raw materials ZnSO_4 , $\text{Tb}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$ were employed as a nominal composition of $\text{Zn}_{0.985}(\text{Tb}_{0.01}\text{Co}_{0.005})\text{O}$. ZnSO_4 , $\text{Tb}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$ solution was added in 10% NH_4HCO_3 solution to form complex precipitates, and then calcined at 350°C for 1 h. TiO_2 -rich CCTO (TCCTO) with the nominal composition of $\text{CaCu}_3\text{Ti}_{4+0.05}\text{O}_{12+0.1}$ was prepared as previously reported.^{15,16} The powders were pre-calcined at 900°C for 2 h. Rare-earth-doped ZnO powders and TCCTO powders were employed as nominal composition of TCCTO: ZnO = 0, 0.2, 0.3, 0.5, abbreviated as ZnO, TCCTOZ-1, TCCTOZ-2, TCCTOZ-3, and then ball milled for 12 h. The dried mixed powders were then pressed into green pellets (12 mm in diameter) with polyvinyl alcohol binder. Finally, the green pellets were sintered at 1100°C for 3 h in air to obtain TCCTO/ZnO composite ceramics.

The phase composition and microstructure of the TCCTO/ZnO composite ceramics were measured by X-ray diffraction

Fig. 1. XRD patterns of the various TCCTOZ ceramics samples.

(XRD) equipment (Rigaku D-Max 3A, Cu K_{α} radiation) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDS). The ceramic samples were polished and pasted by silver paste on both sides, and

then fired at 600°C for 1 h to form the electrodes. The dielectric response was performed by using a HP 4194 grain phase analyzer over the range of frequency from 100 Hz to 2 MHz under an oscillation voltage of 1 V. The nonlinear coefficient and varistor voltage of the samples were measured by current–voltage analyzer.

3. Results and Discussions

Figure 1 shows the phase composition of TCCTOZ ceramic samples sintered at 1100°C for 3 h. The XRD patterns indicate that the main phase of the composite ceramics are the ZnO and CCTO phase, and also a new phase ZnCuTiO₄ can be seen from the XRD patterns. As the additional content of TCCTO increases, the CCTO and ZnCuTiO₄ phase can be seen more clearly, while the ZnO phase decreases, especially in the TCCTOZ-3 sample. In the solid reaction in CCTO–ZnNb₂O₆ system 17, ZnCuTiO₄ can also be seen in the reaction products. Microstructure and EDS analysis shown in Fig. 2 reveal that the small cubic grains (Area A) are CCTO, and the area B are ZnO and ZnCuTiO₄ phases, which are in good agreement with the XRD patterns.

Fig. 2. SEM images of (a) TCCTOZ-1, (b) TCCTOZ-2 ceramics samples, and (c) EDS results of the local phases of the TCCTOZ-2 sample shown in the insets A and B.

Fig. 3. Dielectric properties of TCCTOZ samples at room temperature.

The dielectric properties of different TCCTOZ samples are characterized in Fig. 3 at room temperature in the range of frequency from 100 Hz to 2 MHz. The results indicate the dielectric properties of ZnO can be improved by the addition of TCCTO phase, and the dielectric constant can reach 214 at 1 kHz for the TCCTOZ-2 sample as shown in Table 1, which is much higher than that of rare-earth-doped ZnO varistors ($\epsilon \sim 105$) and that of pure ZnO ($\epsilon \sim 8.6$).⁶ And the dielectric constant of TCCTO and ZnO is about 104 and 59 at 1 kHz as characterized in the experiment with the same sintering process, respectively. Compared to this rare-earth Tb-doped ZnO, the dielectric constant of the composite ceramics was improved greatly and remained at high nonlinear coefficient. With the increase of the amount of the TCCTO, the dielectric constant of TCCTOZ can also increase obviously, which may be due to the addition of high dielectric CCTO phase and the new ZnCuTiO_4 phase.¹⁷ However, the high dielectric constant at low frequency is almost contributed by loss, which may be caused by the space charge polarization due to the inhomogeneous microstructure of the composite ceramics.

We also investigated the current–voltage characteristics of these samples. Figure 4 shows the current–voltage properties of the TCCTOZ ceramics at room temperature. Generally, the correlation between the current and voltage of the varistor ceramics can be determined by the Eq. (1).¹⁸

$$I = kV^\alpha, \quad (1)$$

where α is the nonlinear coefficient, which can determine the nonlinear characteristics of the varistors, and k is a material constant. According to the Eq. (1), the nonlinear exponent α can be calculated by Eq. (2).¹⁹

$$\alpha = d(\ln I)/d(\ln V). \quad (2)$$

And the varistor voltage can be obtained when the current density is 1 mA/cm^2 . Table 1 lists the varistor properties of the samples. Bernik *et al.*²⁰ doped Y_2O_3 in $\text{ZnO-Bi}_2\text{O}_3$ -based

Fig. 4. Current–voltage curves of various TCCTOZ samples at room temperature.

Table 1. Varistor characteristics of various TCCTOZ samples.

Sample	Varistor voltage (V/mm)	Nonlinear coefficient	Dielectric constant (1 kHz)
ZnO	1256	26.0	59
TCCTOZ-1	2241	11.4	103
TCCTOZ-2	1041	10.3	214
TCCTOZ-3	6	2.9	22980

varistor and the nonlinear α is approximately 40. We prepared the ZnO varistor only doped with two additives, rare-earth Tb and Co, and the nonlinear coefficient can reach 26. The results show that TCCTOZ-1 and TCCTOZ-2 exhibit large varistor voltage 2241 and 1041, and the nonlinear coefficient can be 11.4 and 10.3, respectively. The results indicate that TCCTO/ZnO composite ceramics show high dielectric permittivity and tunable varistor behaviors, which can obtain potential applications for higher voltage transportation devices. However, TCCTOZ-3 exhibits low nonlinear exponent and varistor voltage, and the voltage does not decrease continuously, which could be due to the fact that the existing large amount of ZnCuTiO_4 phase in the composite ceramics change the microstructure, and lead to the reduction of the potential barrier at the grain boundary of ZnO and leads to the reduction of the potential barrier at the grain boundary of ZnO.

4. Conclusions

In conclusion, we prepared TCCTO/ZnO composite ceramics by the chemical co-precipitation combined with solid-state sintering method. The dielectric constant of the composite of TCCTO: ZnO = 0.3 reached ~ 210 at 1 kHz, the varistor voltage was 1041 V/mm. and the nonlinear coefficient was 11.4 at room temperature, which potentially makes such

composite ceramics attractive for technological applications for the electric devices.

Acknowledgments

This work was supported by the Ministry of Science and Technology of China through a 973-Project under Grant No. 2009CB623303, NSF of China (50737001, 50972068), NSF of Beijing 2092016 and Scientific Research Project of Tsinghua University No. 2009THZ08063.

References

- ¹P. R. Emtage, Physics of zinc-oxide varistors, *J. Appl. Phys.* **48**, 4372 (1977).
- ²D. R. Clarke, Microstructural location of intergranular metal-oxide phase in a zinc-oxide varistor, *J. Appl. Phys.* **49**, 2407 (1978).
- ³L. M. Levinson and H. R. Philipp, High-frequency and high-current studies of metal-oxide varistors, *J. Appl. Phys.* **47**, 3116 (1976).
- ⁴J. Fan and R. Freer, The electrical-properties and DC degradation characteristics of silver doped ZnO varistors, *J. Mater. Sci.* **28**, 1391 (1993).
- ⁵A. B. Alles and V. L. Burdick, The effect of liquid-phase sintering on the properties of Pr_6O_{11} -based ZnO varistors, *J. Appl. Phys.* **70**, 6883 (1991).
- ⁶J. N. Cai, Y. H. Lin, M. Li, C. W. Nan, J. L. He and F. L. Yuan, Sintering temperature dependence of grain boundary resistivity in a rare-earth-doped ZnO varistor, *J. Amer. Ceram. Soc.* **90**, 291 (2007).
- ⁷M. A. Subramanian, D. Li, N. Duan and B. A. Reisner, A. W. Sleight, High dielectric constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ phases, *J. Solid State Chem.* **151**, 323 (2000).
- ⁸A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt and S. M. Shapiro, Giant dielectric constant response in a copper-titanate, *Solid State Commun.* **115**, 217 (2000).
- ⁹W. Q. Ni, X. H. Zheng and J. C. Yu, Sintering effects on structure and dielectric properties of dielectrics $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, *J. Mater. Sci.* **42**, 1037 (2007).
- ¹⁰J. N. Cai, Y. H. Lin, B. Cheng, C. W. Nan, J. L. He, Y. J. Wu and X. M. Chen, Dielectric and nonlinear electrical behaviors observed in Mn-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic, *Appl. Phys. Lett.* **91**, 252905-1 (2007).
- ¹¹B. Cheng, Y. H. Lin, J. C. Yuan, J. N. Cai, C. W. Nan, X. Xiao and J. L. He, Dielectric and nonlinear electrical behaviors of La-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *J. Appl. Phys.* **106**, 034111-1 (2009).
- ¹²F. C. Luo, J. L. He, J. Hu and Y. H. Lin, Electric and dielectric properties of Bi-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *J. Appl. Phys.* **105**, 076104-1 (2009).
- ¹³Y. H. Lin, J. A. Cai, M. Li, C. W. Nan and J. L. He, High dielectric and nonlinear electrical behaviors in TiO_2 -rich $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *Appl. Phys. Lett.* **88**, 172902-1 (2006).
- ¹⁴Y. H. Lin, J. N. Cai, M. Li, C. W. Nan and J. L. He, Grain boundary behavior in varistor-capacitor TiO_2 -rich $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *J. Appl. Phys.* **103**, 074111-1 (2008).
- ¹⁵P. Jha, P. Arora and A. K. Ganguli, Polymeric citrate precursor route to the synthesis of the high dielectric constant oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, *Mater. Lett.* **57**, 2443 (2003).
- ¹⁶J. J. Liu, Y. C. Sui, C. G. Duan, W. N. Mei, R. W. Smith and J. R. Hardy, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: Low-temperature synthesis by pyrolysis of an organic solution, *Chem. Mater.* **18**, 3878 (2006).
- ¹⁷G. P. Du, W. Li, Y. Fu, N. Chen, C. Q. Yin and M. M. Yan, An investigation on the solid-state reactions in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - ZnNb_2O_6 system, *Mater. Res. Bull.* **43**, 2504 (2008).
- ¹⁸D. R. Clarke, Varistor ceramics, *J. Amer. Ceram. Soc.* **82**, 485 (1999).
- ¹⁹T. K. Gupta, Application of Zinc-oxide varistors, *J. Amer. Ceram. Soc.* **73**, 1817 (1990).
- ²⁰S. Bernik, S. Macek and B. Ai, Microstructural and electrical characteristics of Y_2O_3 -doped $\text{ZnO-Bi}_2\text{O}_3$ -based varistor ceramics, *J. Eur. Ceram. Soc.* **21**, 1875 (2001).