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Short communication

Effect of Ta_2O_5 in (Ca, Si, Ta)-doped TiO_2 ceramic varistors

Shaohua Luo [a,b,*], Zilong Tang [a], Jianying Li [c], Zhongtai Zhang [a]

[a] *State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*
[b] *Department of Materials Science and Engineering, Northeastern University at Qinhuangdao Branch, Qinhuangdao, 066004, China*
[c] *Multi-Disciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an 710049, China*

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Abstract

TiO_2 varistors doped with 0.2 mol% Ca, 0.4 mol% Si and different concentrations of Ta were obtained by ceramic sintering processing at 1350 °C. The effect of Ta on the microstructures, nonlinear electrical behavior and dielectric properties of the (Ca, Si, Ta)-doped TiO_2 ceramics were investigated. The ceramics have nonlinear coefficients of $\alpha = 3.0–5.0$ and ultrahigh relative dielectric constants which is up to 10^4. Experimental evidence shows that small quantities of Ta_2O_5 improve the nonlinear properties of the samples significantly. It was found that an optimal doping composition of 0.8 mol% Ta_2O_5 leads to a low breakdown voltage of 14.7 V/mm, a high nonlinear constant of 4.8 and an ultrahigh electrical permittivity of 5.0×10^4 and tg $\delta = 0.66$ (measured at 1 kHz), which is consistent with the highest and narrowest grain boundary barriers of the ceramics. In view of these electrical characteristics, the TiO_2–0.8 mol% Ta_2O_5 ceramic is a viable candidate for capacitor–varistor functional devices. The characteristics of the ceramics can be explained by the effect and the maximum of the substitution of Ta^{5+} for Ti^{4+}.

Keywords: TiO_2 varistor; Tantalum oxide; Microstructure; Electrical property

1. Introduction

Varistors are known for their application as surge protection devices in power system and also in electronic circuits. Up to now, ZnO-based varistors have been extensively studied. The recent trend in electrical appliance design requires varistors that contain more functions and have a relatively low breakdown voltage, which facilitate the denser integrated circuits. Moreover, the low permittivity of ZnO varistor weakens its ability to absorb the sparks, and therefore restricts its application in the low voltage circuit. The TiO_2-based varistor has attracted much interest in recent years. Yan and Rhodes [1] first reported that (Nb, Ba)-doped TiO_2 ceramics had useful varistor properties with α of about 4. Then TiO_2 ceramics with different dopants added were developed such as: (Pb, Nb)-TiO_2 [2], (Ba, Bi, Nb)-TiO_2 [3], (Cr, Nb)-TiO_2 [4], (Y, Nb)-TiO_2 [5] and (Ca, Si, Ce, Nb)-TiO_2 [6,7]. As above, the 5+ valences Nb is commonly used as the dopant to decrease the lattice resistivity of TiO_2 in most papers. Divalence or trivalence cations with large ionic radii, e.g., alkaline metal segregate at the TiO_2 grain boundaries. The addition of Bi or Pb results in the formation of low-melting component, which redound to create the efficient boundary barrier layer.

Although Ta^{5+} with a valence 5+ and similar ionic radii as Ti^{4+}, which can donate conduction electrons and have a reasonable solubility in the Ti sublattice that of Nb^{5+}, the system of Ta-doped TiO_2 had been few studied. The Ta_2O_5 is also applied in other varistor system such as SnO_2-based varistors [8]. Only mone-doped Ta-TiO_2 [9], binary doped Ta-TiO_2: M (M = Ba [10], Ca [11,12]) ceramics had been studied. The detailed study of system of ternary-doped Ta-TiO_2 has not been reported yet. Meantime, volatility of low-melting component from Bi_2O_3 and PbO during high-temperature sintering causes problems in reproducing high-quality electronic ceramics. So the SiO_2, a stable compound can be used to form low-melting component. In this paper, the nonlinear electrical behavior and dielectric properties of (Ca, Si, Ta)-doped TiO_2 ceramics were studied. In particular, the effects of

* Corresponding author at: State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China. Tel.: +86 1062772623; fax: +86 1062783046.
E-mail address: luosh03@mails.tsinghua.edu.cn (S. Luo).

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Ta dopant on the nonlinear electrical behavior and dielectric properties of the ceramics were also investigated.

2. Experimental

Traditional ceramic process was used to prepare the TiO_2 varistor ceramics. The starting chemicals in the present study were reagent grade TiO_2, Ta_2O_5, SiO_2 and $CaCO_3$. The investigated compositions contained cation ratio of Ti:Si:Ca:-Ta = 100:0.4:0.2:x with x = 0.2, 0.4, 0.6, 1.0, 1.6, 2.0. The chemicals were weighted according to the stoichiometric amount of final composite. The powder mixture was wet ball-milled in a polyethylene bottle with ZrO_2 balls for 4 h in deionized water. The milled mixtures were dried, granulated and pressed into disks at 150 MPa, with diameter of 10 mm and thickness of 1.2 mm. The disks were sintered at 1350 °C for 4 h in air, and then cooled down in furnace. For electrical measurements, silver electrodes were prepared on both surfaces of the sintered pellets at 570 °C for 20 min.

The varistor voltage $V_{0.1\ mA}$ and $V_{1\ mA}$ were measured by using MY-4C meter. α was calculated by the following formula:

$$\alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)} = \frac{1}{\log(V_{1\,mA}/V_{0.1\,mA})} \quad (1)$$

The relative dielectric constant ε and loss $\tan\delta$ were measured with an LCR meter (2-3532-50 LCR HITESTER) in the frequency 1 kHz. The microstructures of the sintered pellets and grain size were observed with SEM (JSM-6460LV) technology. The grain sizes were determined by the intercept method.

3. Results and discussion

The X-ray powder diffraction patterns of all samples with different concentrations of Ta are similar (Fig. 1). The analysis of the patterns indicates that no other phase except TiO_2 rutile phase exists in the samples. Therefore, CaO and Ta_2O_5 should form a solid solution in TiO_2 when the disks were sintered. If the dopants are dissolved into rutile lattice, the defect equations can be expressed as follows using Kroger–Vink notation:

$$Ta_2O_5 \xleftrightarrow{TiO_2} 2Ta_{Ti}^{\bullet} + 2e' + 4O_O^X + \tfrac{1}{2}O_2\uparrow \quad (2)$$

$$CaO \xleftrightarrow{TiO_2} Ca_{Ti}'' + V_O^{\bullet\bullet} + O_O^X \quad (3)$$

Since Ta has an ionic radius similar to that of Ti, it easily dissolves into the TiO_2 lattice. According to Eq. (2), the dissolution of Ta into TiO_2 grains will introduce free electrons and positive charge defects ($Ta_{Ti}^{\bullet}$). Due to the generation of electrons, the free electron concentration in the TiO_2 grains is increased. Thus, the resistivity of TiO_2 grains is decreased. On the other hand, the dissolution of Ca into TiO_2 lattice creates one oxygen vacancy and negatively charged defect (Ca_{Ti}'') according to Eq. (3). Comparing Ti^{4+} (0.61 Å) with Ca^{2+} (1.01 Å), the Ca^{2+} with a larger ionic radius and a lower valence prefers to segregate at grain boundaries in order to relieve the great elastic strain energy caused by ionic radius mismatch. So Ca has a very low solubility in the TiO_2 grains. Hence, only a small quantity of Ca added dissolves into TiO_2 grains while most of Ca segregate at grain boundaries.

The typical SEM micrograph of the (Ca, Ta)-doped TiO_2 varistor is shown in Fig. 2, which is characterized by heterogeneous grains with average grain size (d_g) of several microns. Clearly, there is no apparent second phase observed in the SEM micrograph. The average grain size (d_g) of each sample, calculated by the intercept method, slowly decreases from 3.77 to 2.08 μm with increasing of the doping concentration of Ta from 0.2 to 2.0 mol%.

The $V_{1\ mA}$ and α curves for samples doped with different concentrations of Ta are given in Fig. 3. It can be seen from Fig. 3 that $V_{1\ mA}$ decreases sharply with increase of Ta_2O_5, which is similar to the general reported results. In this process, free electrons can be released from the substitution of Ti^{4+} with Ta^{5+} when the Ta addition varies from 0.2 to 1.6 mol%. It is also found that the nonlinear coefficient α increases from 3.2 to 4.8 at the same time. Thus, the substitution of Ti^{4+} with Ta^{5+} cannot only decrease the grain resistance by more free electrons, but

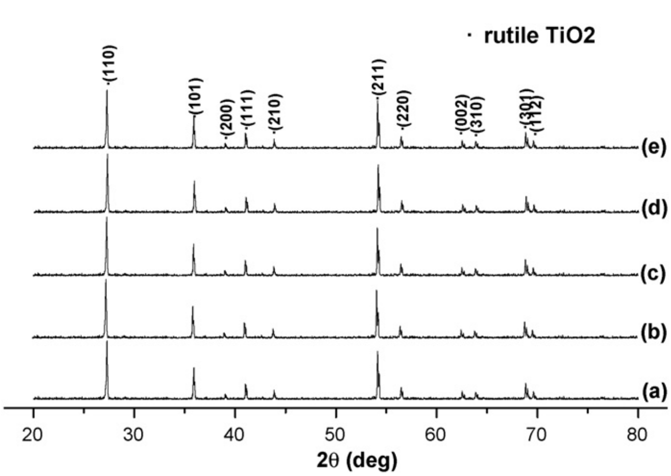

Fig. 1. X-ray powder diffraction patterns of samples doped with different concentrations of Ta: (a) x = 0.2; (b) x = 0.4; (c) x = 0.6; (d) x = 1.0; (e) x = 2.0.

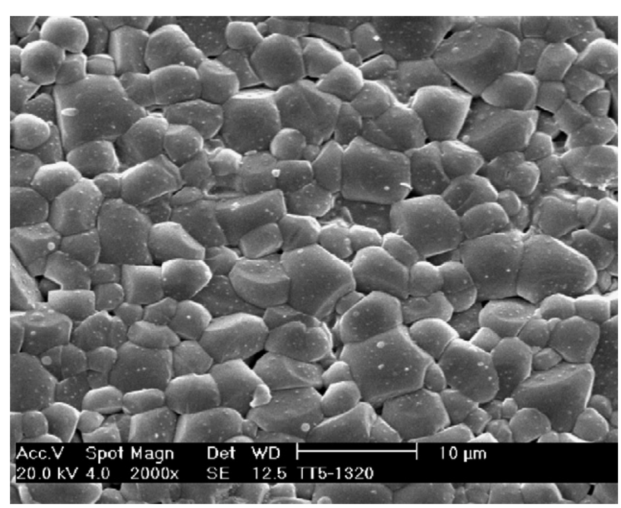

Fig. 2. Typical SEM micrograph of samples.

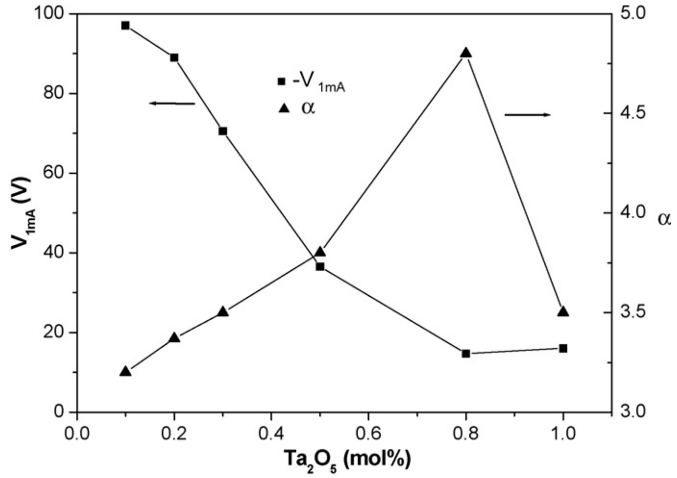

Fig. 3. $V_{1\ mA}$ and α vs. the content of Ta_2O_5 dopant.

also leads to a high grain boundary barrier and, consequently, high α value. The sample doped with 0.8 mol% Ta_2O_5 exhibits the highest nonlinear coefficient and the lowest breakdown voltage. However, the substitution of Ta^{5+} for Ti^{4+} exists a maximum value. When the dopant Ta_2O_5 exceeds 0.8 mol%, the nonlinear characteristic α rapidly drops from 4.8 to 3.5. As regards to $V_{1\ mA}$, it rises slightly from 14.7 to 16. The superfluous Ta^{5+}, which cannot substitute Ti^{4+} further, will segregate to grain boundary interface. The segregation of Ta^{5+} blocks the formation and transportation of e^- and other defects, which will play an effect on the properties of the TiO_2-based ceramics contrary to the substitution of Ta^{5+} for Ti^{4+}. The increasing of Ta addition results in the deterioration of nonlinear property and rising of $V_{1\ mA}$.

Fig. 4 shows the relative dielectric constant (ε_γ) and tan δ with different concentrations of Ta. Obviously, the ε_γ value and tan δ exhibit similarly peak-like tendency with increasing of Ta content. It is shown that the 0.8 mol% Ta_2O_5 specimen possesses two highest values, 4.99×10^4 for ε_γ and 0.66 for tan δ. Higher effective relative dielectric constant and dissipation factor can be attributed to significant electronic conduction. The low-resistivity surface layer increases the dissipation factor of the sample especially in the low-frequency 1 kHz region where electron motion is possible. It is also believed that the increase of the effective relative dielectric constant in the low frequency region usually results from conduction loss. When the concentration of Ta_2O_5 dopant is up to 0.8 mol%, the rising tendency obtains its maximum value.

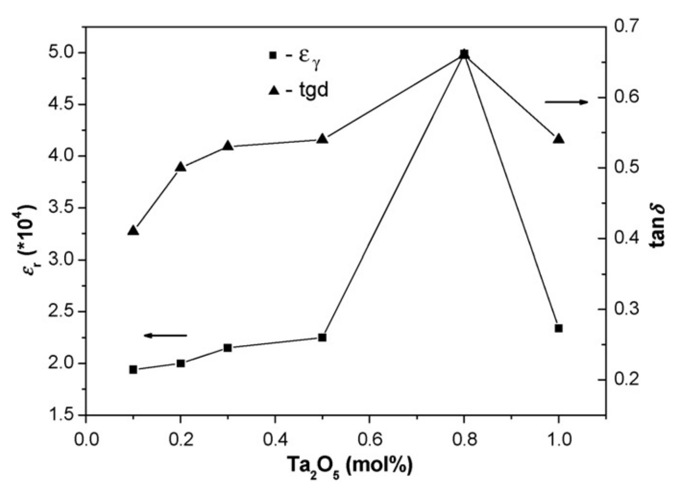

Fig. 4. Effective relative dielectric constant and tan δ vs. the content of Ta_2O_5 dopant.

4. Conclusions

The Ta dopant has significant effects on the nonlinear electrical behavior and dielectric properties of the (Ca, Si, Ta)-doped TiO_2 varistors. An optimal doping composition of (0.8Ta, 0.4Si, 0.2Ca)-doped TiO_2 was obtained with a low $V_{1\ mA}$ of 14.7 V, a high nonlinear constant of 4.8, an ultrahigh electrical permittivity of 4.99×10^4 and higher dissipation factor 0.66 (measured at 1 kHz), which can be used as capacitor–varistor ceramics. Deviations from this doping composition, towards either higher or lower Ta_2O_5 contents, cause deterioration of the *I–V* nonlinear characteristics. There is a correlation between the nonlinear electrical and dielectric properties of the (Ca, Si, Ta)-doped TiO_2 varistors.

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References

[1] M.F. Yan, W.W. Rhodes, Preparation and properties of TiO_2 varistors, Appl. Phys. Lett. 40 (6) (1982) 536–537.
[2] J.M. Wu, C.H. Lai, Effect of lead oxide on niobium-doped titania varistors, J. Am. Ceram. Soc. 74 (1991) 3112–3117.
[3] S.L. Yang, J.M. Wu, Novel niobium-doped titania varistors with barium and bismuth, J. Am. Ceram. Soc. 76 (1993) 145–152.
[4] P.R. Bueno, E. Camargo, E. Longo, E. Leite, S.A. Pianaro, J.A. Varela, Effect of Cr_2O_3 in the varistor behavior of TiO_2, J. Mater. Sci. Lett. 15 (1996) 2048–2050.
[5] C.P. Li, J.F. Wang, X.S. Wang, W.B. Su, H.C. Chen, D.X. Zhuang, Nonlinear electrical properties of TiO_2–Y_2O_3–Nb_2O_5 capacitor–varistor ceramics, Mater. Sci. Eng. B 85 (2001) 6–10.
[6] S.H. Luo, W.W. Yao, H.Y. Li, Z.L. Tang, Z.T. Zhang, X.Z. Xiong, The role of niobium in (Ca, Si, Ce, Nb)-doped TiO_2 varistors, Key Eng. Mater. 280–283 (2005) 297–300.
[7] S.H. Luo, W.W. Yao, H.Y. Li, J.P. Yan, Z.L. Tang, Z.T. Zhang, X.Z. Xiong, Effect of CeO_2 on electric properties of TiO_2 based capacitor–varistor multi-function ceramics, Rare Metal Mater. Eng. 33 (7) (2004) 748–751.
[8] F.M. Filho, A.Z. Simoes, A. Ries, I.P. Silva, L. Perazolli, E. Longob, J.A. Varela, Influence of Ta_2O_5 on the electrical properties of ZnO- and CoO-doped SnO_2 varistors, Ceram. Int. 30 (2004) 2277–2281.
[9] C.P. Li, J.F. Wang, X.S. Wang, H.C. Chen, W.B. Su, Nonlinear electrical properties of Ta-doped titania capacitor–varistor ceramics, Mater. Chem. Phys. 74 (2002) 187–191.
[10] A.B. Gaikwad, S.C. Navale, V. Ravia, TiO_2 ceramic varistor modified with tantalum and barium, Mater. Sci. Eng. B 123 (2005) 50–52.
[11] W.Y. Wang, D.F. Zhang, T. Xu, X.F. Li, T. Zhou, X.L. Chen, Nonlinear electrical behavior and dielectric properties of (Ca, Ta)-doped TiO_2 ceramics, J. Alloys Compd. 335 (2002) 210–215.
[12] W.Y. Wang, D.F. Zhang, X.L. Chen, Nonlinear electrical behavior and dielectric properties of (Ca, Ta)-doped TiO_2 ceramics, J. Mater. Sci. 38 (2003) 2049–2054.