

# Origin of the varistor properties of terbium oxide ceramics

XIU-FANG WANG, YU WANG<sup>a</sup>

*EMei Campus, Southwest Jiaotong University, EMei 614202, China*

<sup>a</sup>*School of Electrical Engineering, Southwest Jiaotong University, Chengdu 610031, China*

The ceramic samples were prepared using the standard ceramic method and sintered in air at 1300 °C for 2 h. The fabricated samples were subjected to subsequent heat treatment in different atmospheres to study the physical origin of the nonlinear electrical properties. Heat treatment in a reducing atmosphere decreases the nonlinear electrical properties of the samples. However, repeating the heat treatment in an oxidizing atmosphere can recover the electrical properties to nearly its original value. It is proposed that the adsorbed oxygen on grain surfaces plays a key role in governing the varistor properties. The physical origin is an intrinsic characteristic of pure terbium oxide ceramics, which is different from that of the varistors reported previously. The change of the electrical properties can be attributed to the variation in the amount of adsorbed oxygen on the grain surfaces.

(Received October 1, 2012; accepted June 12, 2013)

*Keywords:* Varistor, Terbium oxide, Heat treatment, Oxygen adsorption

## 1. Introduction

Varistors are materials with unique non-linear, current-voltage characteristics that allow them to be employed in voltage surge protection applications. Today, the majority of varistors produced commercially are based on ZnO with minor additions of typically Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, CoO, MnO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> [1-3]. A new varistor system based on SnO<sub>2</sub> has been reported by Pianaro in 1995 [4]. At the same time, other varistor systems have been studied, because of the need for even better properties. Among them, systems based on SrTiO<sub>3</sub> [5], TiO<sub>2</sub> [6] and WO<sub>3</sub> [7] have been reported in the literature.

The nonlinear current-voltage characteristic of the varistors is understood to be result from the back-to-back Schottky barriers at the grain boundaries. According to the barrier formation model for metal oxide varistor systems, the physical origin of the varistor properties is not an intrinsic one caused by lattice mismatch at the boundaries, but an extrinsic one resulting from metal atoms segregated at the grain boundaries [8-14]. These metal atoms, such as Bi in ZnO-based varistors or Mn and Co in SnO<sub>2</sub>-based varistors, facilitate the adsorption of oxygen on the grain surfaces [8-13]. Although these varistors have been widely studied, still there are some important problems remain unclear. For example, physical origin of interface states, precise mechanism of degradation and actual breakdown phenomenon of the Schottky barriers [3, 15-17]. The traditional varistors are not suitable for studying these problems due to the complicated structures caused by various additives, so a new varistor system with no

additives is needed. More recently, pure terbium oxide ceramics has been investigated by our research group and nonlinear electrical properties were observed in this ceramics [18]. The simple microstructure, consisting generally in one phase under X-ray resolution, is the main characteristic of this ceramics. In order to research the physical origin of terbium oxide varistor, samples sintered in air were heat treated in Ar and then further treated in an oxygen rich atmosphere.

## 2. Experimental procedure

Samples were prepared by conventional ceramics techniques. The raw material in this study was Tb<sub>4</sub>O<sub>7</sub> (purity ≥ 99.95%, YueLong Inc., China). After milling in an agate mortar for 3 h, the powder was calcined in air at 800 °C for 2 h. The powder was then granulated with 2 % by weight polyvinyl alcohol binder and pressed at 100 MPa to form discs 10 mm in diameter and 1.0–1.5 mm in thickness. The pressed discs were sintered at 1300 °C in air for 2 h. The sintered samples were heat treated in Ar (99.9%) (under a flux of 20 cm<sup>3</sup>/min) and further treated in O<sub>2</sub> (99.9%) (under flux of 20 cm<sup>3</sup>/min) atmosphere at 900 °C for 1 h. The phase constitutions were determined by x-ray diffraction (XRD, 7602EA ALMELO) with a Cu K<sub>α</sub> radiation of 0.154060 nm in wavelength. A scanning electron microscope (SEM, FEI QUANTA200) with a 20 kV operating voltage was used to observe the grain size and shape of the samples. For electrical measuring, In–Ga mixed alloy (the purity of both are 99.999%, In:Ga = 1:1)

as electrode material was painted on both polished surfaces of samples. The electrode area was  $72 \text{ mm}^2$ . The current-voltage ( $I$ - $V$ ) characteristics of the sample were measured using a Keithley 2400. The microstructure and electrical behavior were checked after each treatment.

### 3. Results and discussion

The XRD patterns for the ceramic samples after each treatment are shown in Fig. 1. The diffraction peaks are indexed based on  $\text{Tb}_4\text{O}_7$  fluorite structure. From the obtained X-ray data, it can be observed that all patterns are identical indicating no crystal phase changes after heat treatment in different atmospheres. The SEM images of the samples are also almost the same after heat treatment.

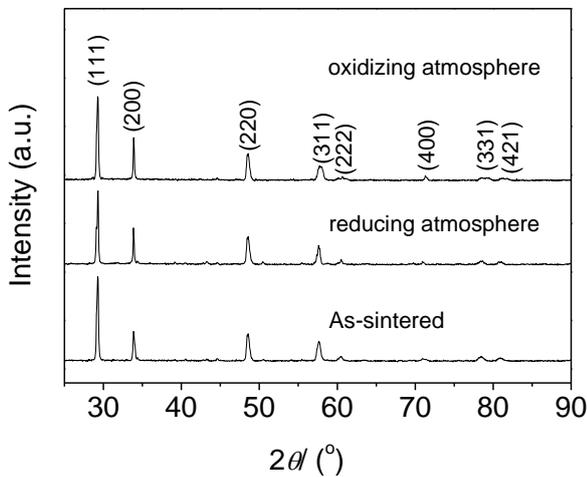


Fig. 1. XRD patterns of the ceramic samples.

Fig. 2 shows current-voltage characteristics of the samples heat treated in different atmospheres. The current

sharply increases when it exceeds  $10 \text{ mA/cm}^2$ , so we can define the breakdown voltage as the electrical field corresponding to  $I = 10 \text{ mA/cm}^2$ . The nonlinear coefficient  $\alpha$  was calculated by

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

where  $V_1$  is the voltage corresponding to  $I_1 = 10 \text{ mA/cm}^2$ , and  $V_2$  to  $I_2 = 100 \text{ mA/cm}^2$ , respectively. The values of nonlinear coefficient and breakdown voltage are listed in Table 1. Here, it can be shown the reversibility of the nonlinear coefficient obtained from  $I$ - $V$  curves after heat treatment in reducing atmosphere and again in oxidizing atmosphere. The same behavior is obtained concerning breakdown voltage values of the samples.

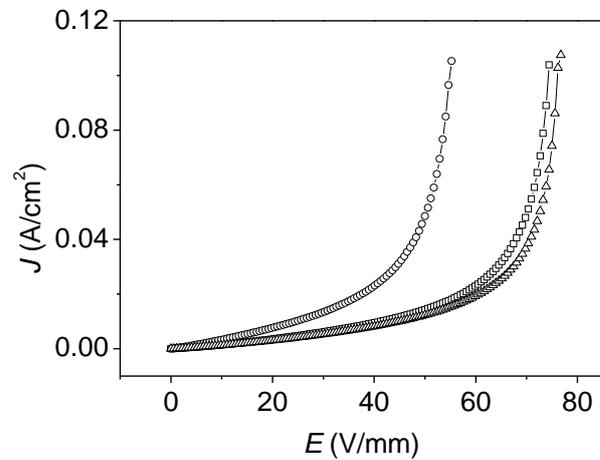


Fig. 2. Current-voltage characteristics of the samples heat treated in different atmospheres: ( $\square$ ) as-sintered, ( $\circ$ ) reducing, ( $\triangle$ ) oxidizing.

Table 1. Some electrical parameters of  $\text{Tb}_4\text{O}_7$ -based varistors.

sample	$\alpha$	$E_b$ (V/mm)	$\Phi_B$ eV	$N_d$ $10^{27}/\text{m}^3$	$N_s$ $10^{18}/\text{m}^2$	$w$ $\text{\AA}$
as-sintered	3.9	40	0.20	6.42	2.06	1.61
reducing atmosphere	2.8	25	0.15	6.30	1.79	1.42
oxidizing atmosphere	4.3	45	0.22	6.30	2.13	1.69

In order to research the change of electrical properties of the samples treated in different atmosphere, barrier parameters were measured after each treatment. Since the effective cross-sectional area of conduction across the grain-boundary barriers is not precisely determined for low density  $\text{Tb}_4\text{O}_7$  ceramics [19], the  $C$ - $V$  method of

extracting the device-related parameters is limited. The values for potential barrier parameters were determined using  $I$ - $V$  curves for different temperatures [20] and the Schottky thermionic emission model given by the equation:

$$J = A^* T^2 \exp \left[ \frac{\beta V^{1/2} - \Phi_B}{k T} \right] \quad (2)$$

where  $A^*$  is Richardson's constant,  $\Phi_B$  the interface barrier height,  $k$  Boltzmann constant, and  $\beta$  a constant related to the grain size and the barrier width. The constant  $\beta$  is given by

$$\beta = \left[ \left( \frac{1}{nw} \right) \left( \frac{2e^3}{4\pi\epsilon_0\epsilon_r} \right) \right]^{1/2} \quad (3)$$

where  $n$  is the number of grains in series,  $w$  is the barrier width,  $e$  is the electron charge,  $\epsilon_0$  and  $\epsilon_r$  are the vacuum and material dielectric constant ( $\epsilon_r = 30$ ) [21], respectively,  $n$  is defined by

$$n = \frac{L}{G} \quad (4)$$

where  $L$  is the sample height and  $G$  is the mean grain size determined from the scanning electron micrographs. To obtain the values of  $w$  and  $\Phi_B$ , Eq. (2) is converted to

$$\ln J = \ln AT^2 + \frac{\beta V^{1/2} - \Phi_B}{k_B T} \quad (5)$$

According to Eq. (5) there is a linear relationship between  $\ln J$  and  $V^{1/2}$  with slope given by  $\beta/KT$ . Fig. 3 shows the plot of  $\ln J$  versus  $V^{1/2}$  at different temperatures for the as-sintered sample. Parallel straight lines are observed for the electric field and temperature range studied. The results suggest thermionic emission as the conduction mechanism in this  $Tb_4O_7$  based varistor system. The model for the barrier at the grain boundaries belong to Schottky type. A similar behavior was observed in samples after heat treatment in different atmospheres. The barrier width can be deduced from the slope of  $\ln J$  versus  $V^{1/2}$ . By extrapolating the plots to  $V = 0$ , the intersection of the extrapolated line with the axis of  $\ln J$  can be obtained for all samples. Then, from the value of the intercept, the values of  $\Phi_B$  can be derived. Donor density ( $N_d$ ) and surface state density ( $N_s$ ) can be derived from the equation  $\Phi_B = e^2 N_s^2 / 2\epsilon_0\epsilon_r N_d$  and  $N_s = 2wN_d$ . The corresponding parameters are listed in Table 1. The values of barrier height, surface state density and barrier width are reversible with the change of heat treatment atmospheres, the donor density does not has obvious change. From the results, it can be seen that oxidizing atmosphere has an important influence on the barrier height.

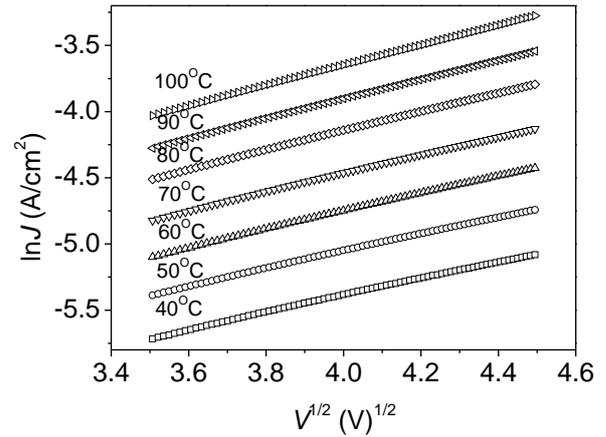


Fig. 3.  $\ln J$  as a function of  $V^{1/2}$  for the sample sintered in air at 1300 °C for 2 h.

Terbium oxide ( $TbO_x$ ) has different oxygen compositions with  $x$  ranging from 1.5 to 2.0 due to the multiple oxidation states (+3 and +4) of Tb [22]. It can release oxygen with the increase of ambient temperature and then incorporate oxygen in the process of cooling. Grain oxidation first occurs and then oxygen adsorption takes place on the grain surfaces when below a certain temperature [14]. In the process of oxidizing, a fully oxidized stoichiometric grain is notoriously difficult to prepare and the grain is still semiconducting [23], so the potential barriers of the terbium oxide varistor should be attributed to oxygen adsorption. The adsorbed oxygen may easily capture electrons to become negatively charged ions. To maintain the electrical neutrality, the negative charges on the grain boundary are balanced on both sides by the electron-depleted space-charge layers in the adjacent grains. As a result, double Schottky barriers are formed at the junctions. Terbium oxide is a good oxygen-ion conductor [22], the interstitial Tb ions can easily combine with oxygen from the ambient to form terbium oxide, so we suggest that oxygen vacancy would be the main defect in the grain interior.

Heat treatment in reducing atmosphere lead to partial desorption of oxygen adsorbed on the grain surfaces and consequently to a reduction of the interface states density. However, the donor density does not have obvious change. According the equation  $\Phi_B = e^2 N_s^2 / 2\epsilon_0\epsilon_r N_d$ , the barrier height will reduce after thermal treatment in reducing atmosphere. In the process of further heat treatment in oxidizing atmosphere, grain surfaces can absorb oxygen from the ambient thereby increasing the surface states density. The barrier height would have obvious increase and the nonlinear electrical properties were recovered.

#### 4. Conclusions

The physical origin of terbium oxide varistor was investigated by means of heat treatment. The nonlinear

coefficient first decreases and then increases when treated in different atmospheres. It is proposed that the varistor properties are derived from the adsorbed oxygen on the grain surfaces. The change of the electrical properties can be attributed to the variation in the amount of adsorbed oxygen on the grain surfaces.

### Acknowledgements

This work was supported by “Chunhui Project” of Ministry of Education of China (Z2011120) and Fundamental Research Funds for the Central Universities of China (SWJTU2011BR018).

### References

- [1] T. K. Gupta, *J. Am. Ceram. Soc.* **73**(7), 1817 (1990).
- [2] D. R. Clarke, *J. Am. Ceram. Soc.* **82**(3), 485 (1999).
- [3] K. Eda, *IEEE. Elec. Ins. Mag.* **5**(6), 28 (1989).
- [4] S. A. Pianaro, P. R. Bueno, E. Longo, J. A. Varela, *J. Mater. Sci. Lett.* **14**(10), 692 (1995).
- [5] N. Yamaoka, M. Masuyama, M. Fukui, *Am. Ceram. Soc. Bull.* **62**(6), 698 (1983).
- [6] S. L. Yang, J. M. Wu, *J. Mater. Res.* **10**(2), 345 (1995).
- [7] V. Makarov, M. Trontelj, *J. Mater. Sci. Lett.* **13**(13), 937 (1994).
- [8] T. K. Gupta, W. G. Carlson, *J. Mater. Sci.* **20**(10), 3487 (1985).
- [9] Y. Yano, Y. Takai, H. Morooka, *J. Mater. Res.* **9**(1), 112 (1994).
- [10] F. Stucki, F. Greuter, *Appl. Phys. Lett.* **57**(5), 446 (1990).
- [11] P. R. Bueno, M. R. Cassia-Santos, E. R. Leite, E. Longo, J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, *Appl. Phys.* **88**(11), 6545 (2000).
- [12] P. R. Bueno, M. M. Oliveira, W. K. Bacelar-Junior, E. R. Leite, E. Longo, G. Garcia-Belmonte, J. Bisquert, *J. Appl. Phys.* **91**(9), 6007 (2002).
- [13] P. R. Bueno, E. R. Leite, M. M. Oliveira, M. O. Orlandi, E. Longo, *Appl. Phys. Lett.* **79**(1), 48 (2001).
- [14] Y. Nakano, N. Ichinose, *J. Mater. Res.* **5**(12), 2910 (1990).
- [15] W. P. Chen, S. G. Lu, H. L. W. Chan, *Mater. Sci. Eng. B* **99**(1-3), 70 (2003).
- [16] N. Ohashi, K. Kataoka, T. Ohgaki, *Mater. Trans.* **50**(5), 1060 (2009).
- [17] C. Tsonos, A. Kanapitsas, D. Triantis, *Ceram. Inter.* **37**(1), 207 (2011).
- [18] T. Y. Li, H. W. Zhao, L. Dong, N. Guo, Y. Wang, *J. Phys. D: Appl. Phys.* **42**, 035401 (2009).
- [19] M. A. Alim, *J. Appl. Phys.* **78**(7), 4776 (1995).
- [20] E. R. Leite, J. A. Varela, E. Longo, *J. Mater. Sci.* **27**, 5325 (1992).
- [21] Y. G. Fedorenko, L. A. Otavina, S. V. Korenyuk, *Tech. Phys. Lett.* **26**(10), 916 (2000).
- [22] Z. C. Kang, L. Eyring, *J. Sol. St. Chem.* **155**(1), 129 (2000).
- [23] D. M. Gruen, W. C. Koehler, J. J. Katz, *J. Am. Chem. Soc.* **73**(4), 1475 (1951).

---

\*Corresponding author: wangxiufanghappy@163.com