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Low voltage varistors based on CeO_2

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Abstract

The nonlinear current (*I*)–voltage (*V*) characteristics of cerium dioxide containing few dopants such as a donor (Nb_2O_5 or Ta_2O_5 (0.5 at.%) and a rare earth element oxide (La_2O_3) or alkaline earth element oxide (BaO) (0.5 at.%) shows promising values of nonlinear coefficient (α) values (~5–6) with very low breakdown voltages (E_B ~10–20 V mm^{-1}). The pentavalent tantalum or niobium acts as donor and increases the electronic conductivity. The oxygen adsorbed at the grain boundary acceptors states during sintering and cooling leads to the formation of grain boundary barrier.

Keywords: Ceramics; Doping effects; Schottky barrier

1. Introduction

CeO_2-based oxide materials find wide applications in fuel cells, gas sensors and as a promoter in three-way catalyst (TWC) for automotive exhaust control [1,2]. The ability of CeO_2 for promotion of water gas shift reaction, thermal stability and its oxygen storage capacity makes it an ideal promoter in TWC formulations [3]. The key to oxygen storage capacity of CeO_2-based materials is due to its characteristic feature to shift between Ce^{4+} and Ce^{3+} in the stable cubic fluorite structure, which in fact allows release and transport of O^{2-} ions. Varistors are electroceramic devices that show nonlinear electrical property [4,5]. They are widely used to protect electrical and electronic equipment against transient overvoltages. The most commonly used commercial varistors are ZnO-based compositions [6]. It had been also already well established that the electrical nonlinearity in polycrystalline ZnO ceramics arises from grain boundary phenomenon. Though ZnO shows excellent varistor property, the drawback is its high breakdown field [6]. Low voltage varistors based on $SrTiO_3$ [7] and SnO_2–TiO_2 systems [8–10] have already been reported in the literature. In the case of SnO_2–TiO_2 solid solution, the samples were heated at 1723 K to obtain large grain growth (>15 μm) and α values are in the range of 7–9. However, until now there is no report on low-voltage varistor based on CeO_2 system. There is also no report regarding variation of the resistivity with different donors for CeO_2 system. Recently, we have reported the influence of various donors on the nonlinear electrical characteristics of tin dioxide system [11]. Here we communicate the varistor characteristics of doped cerium dioxide with low breakdown fields.

2. Experimental

Samples are prepared by standard ceramic technique. CeO_2 and Ta_2O_5 (or Nb_2O_5) are weighed in required ratios ($(100 - X)CeO_2 + X$ (Ta or Nb), where $X = 0.01$, 0.05, 0.1 and 0.5, all in at.%) and ($99CeO_2 + 0.5Ta + 0.5Ba$ (or La), all are in at.%) mixed well with acetone and ground for several hours with a agate mortar and pestle. The powder samples are mixed with few drops of a binder (polyvinyl alcohol, 1 wt.% solution) and pelletized (15 mm diameter, 2 mm thickness). The green pellets were sintered at 1573 K for 4 h. The density of the pellets was measured by Archimedes method and they are >93%. The sintered pellets were polished and ohmic silver contacts were obtained by

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curing Ag paste and annealed at 873 K for 30 min. The structure related phase determination was studied by Philip 1730 X-ray diffractometer. The *I–V* characteristics were measured by using Keithley electrometer 6517A. It also contains a built in 1 kV dc power supply so that there is no need of external power supply in the circuit. The current–voltage relation of a varistor is given by the equation,

$$J = \left(\frac{E}{C}\right)^{\alpha} \quad (1)$$

where J is the current density, E is the applied field, C is the proportionality constant and α is the nonlinear coefficient. The current–voltage curves were plotted on log–log scale from which the slope of the curve gives the value of α. The important parameter, E_B breakdown voltage is taken as the field applied when current flowing through the varistor is 1 mA/cm^2. Since Schottky type grain boundary barriers exist in the present samples the current density in ohmic region of varistor is related to the electric field and the temperature given by Eq. [11].

$$J = AT^2 \exp\left[\frac{\beta E^{1/2} - \Phi_B)}{kT}\right] \quad (2)$$

where A, equal to 4 $\rho emk^2/h^3$, is the Richardson's constant, ρ is the density of cerium dioxide, e is the electron charge, m is electron mass, k is the Boltzmann constant, h is the Plank constant, Φ_B is the interface barrier height, and β is a constant related to the relationship

$$\beta \sim \frac{1}{r\omega} \quad (3)$$

where r is the grain number per unit length and ω is the barrier width. Measuring the current density in ohmic region and keeping the temperature of the tested varistor constant, for two different applied fields, the equations are;

$$J_1 = AT^2 \exp\left[\frac{(\beta E_1^{1/2} - \Phi_B)}{kT}\right] \quad (4)$$

$$J_2 = AT^2 \exp\left[\frac{(\beta E_2^{1/2} - \Phi_B)}{kT}\right] \quad (5)$$

The values of Φ_B and β can be calculated from the above equations.

3. Results and discussion

Fig. 1 shows the X-ray diffractogram (XRD) recorded for the present sample. No second phases are found and all the lines are corresponding to CeO_2 cubic phase. It is also to be noted that the concentrations of dopants added are too small to be detected by X-rays. Hence XRD did not reveal any changes due to these dopants. The unit cell parameter (a) calculated by the least square fit is 5.41 Å. The unit cell parameter did not change (up to second decimal accuracy) with minor dopant additions. The variation of room temperature resistivity with different donors content is depicted in Fig. 2. The resistivity decreases continuously for both tantalum- and niobium-doped samples. The incorporation of either tantalum or niobium increases electronic conductivity of cerium dioxide. The defect reaction may be given as

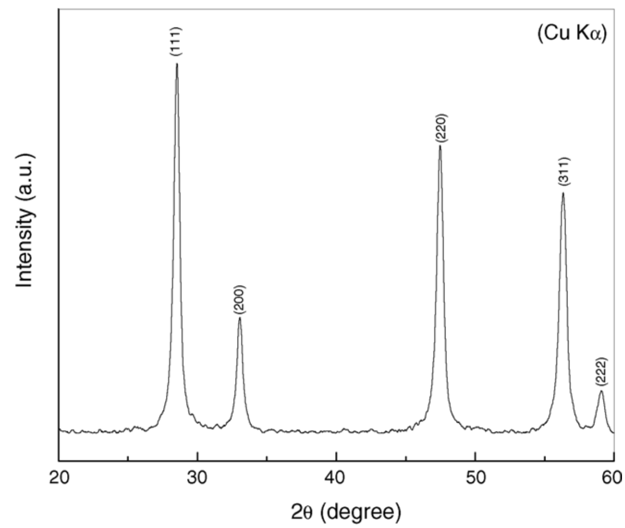

Fig. 1. XRD diagram of 0.5 at.% Ta and 0.5 at.% La co-doped CeO_2 ceramics.

$$Ta_2O_5 \overset{CeO_2}{\rightarrow} 2Ta^{\cdot}_{Ce} + 2e' + 4O^x_{O^{\cdot}} + \tfrac{1}{2}O_2 \quad (6)$$

However, when antimony is added in small quantities to CeO_2 the resistivity does not increase as in the case other donors. This may be due to variable valency of antimony ion and by the different compensation mechanism as explained in Ref. [11]. The *I–V* curves for the samples containing various dopants are illustrated in Fig. 3. The calculated α value for Ta and BaO-doped CeO_2 is 5 and for Ta- and

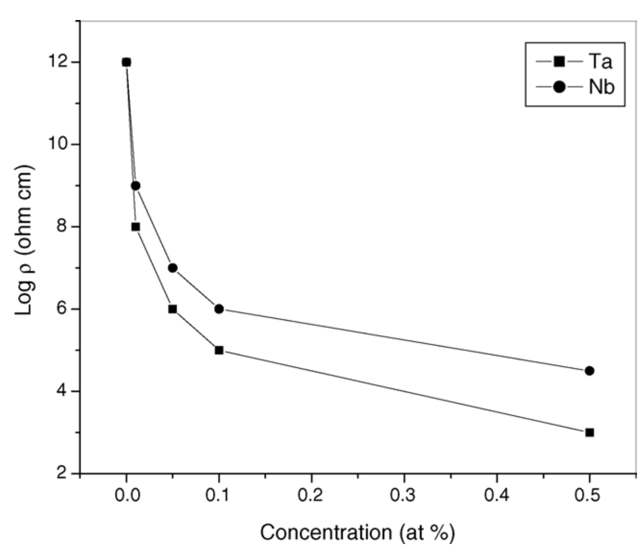

Fig. 2. Variation of the room temperature resistivity with donor content for CeO_2.

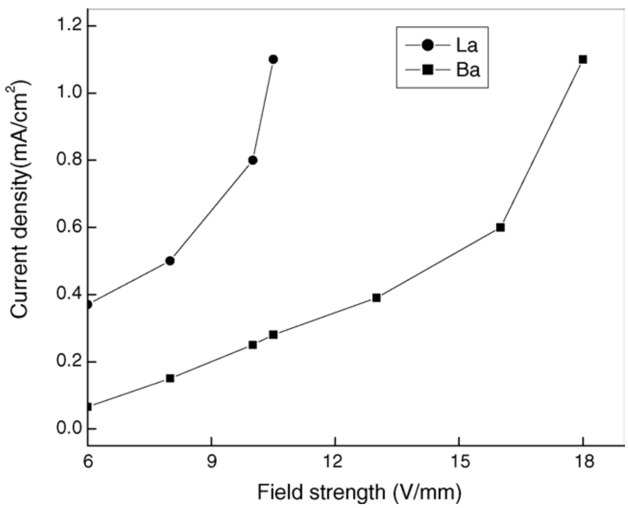

Fig. 3. The *I–V* characteristics of CeO_2 doped with 0.5 at.% Ta + 0.5 at.% Ba and 0.5 at.% Ta + 0.5 at.% La.

La_2O_3-doped CeO_2 is 6 and their breakdown fields are in the range of 10–20 V mm^{-1} as shown in the Fig. 3. The varistor action observed in polycrystalline ZnO ceramics is explained by the presence of Schottky type energy barrier at the grain boundaries. In the present case the acceptor like surface states formed by the oxygen adsorbed at the grain boundary acceptors states during sintering and cooling. This is similar to tin dioxide system reported by us [5] recently, wherein the presence of rare earth ion at the grain boundaries leads to formation grain boundary defect states. There the ionic radius of La^{3+} ion being larger than Sn^{4+} ion, it prefers grain boundary site. However, this modification resulted in high α and E_B values in tin dioxide. This excess oxygen released will be adsorbed by the acceptor states present at the grain boundaries leading to the formation of a barrier. The barrier height calculated for the above samples are in the range of 0.15–0.2 eV.

4. Conclusions

Varistor with low breakdown voltages ($E_B \sim 40$ V/mm) are obtained for doped cerium dioxide system. Both donors Ta and Nb induce semiconductivity in CeO_2 at low concentrations.

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References

[1] S.R. Dhage, S.P. Gaikwad, P. Muthukumar, V. Ravi, Synthesis of $Ce_{0.75}Zr_{0.25}O_2$ by citrate gel method, Mater. Lett. 58 (2004) 2704–2706.
[2] S.R. Dhage, S.P. Gaikwad, P. Muthukumar, V. Ravi, Synthesis of $Ce_{0.75}Zr_{0.25}O_2$ at 100 °C, Ceram. Int. 31 (2005) 211–213.
[3] S. Rossignol, Y. Madier, D. Duprez, Preparation of zirconia–ceria materials by soft chemistry, Catal. Today 50 (1999) 261–270.
[4] V. Ravi, S.K. Date, Nonlinear *I–V* characteristics of doped $Sn_{1-x}Ti_xO_2$ ($0 < x < 0.25$) system, Bull. Mater. Sci. 24 (2001) 483–485.
[5] S.R. Dhage, V. Ravi, S.K. Date, Influence of lanthanum on the nonlinear *I–V* characteristics of SnO_2: Co, Nb, Mater. Lett. 57 (2002) 727–729.
[6] D.R. Clarke, Varistor ceramics, J. Am. Ceram. Soc. 82 (1999) 485–502.
[7] Y. Nakano, N. Ichinose, J. Mater. Res. 5 (1990) 2910.
[8] M.F. Yan, W.W. Rhodes, Preparation and properties of TiO_2 varistors, Appl. Phys. Lett. 40 (1982) 536–537.
[9] P.R. Bueno, M.R. Cassia-Santors, L.G.P. Simoes, J.W. Gomes, E. Longo, J. Am. Ceram. Soc. 85 (2002) 282.
[10] W.B. Su, J.F. Wang, H.C. Chen, W.X. Wang, G.Z. Zhang, C.P. Li, J. Appl. Phys. 92 (2002) 4779.
[11] S.R. Dhage, V. Ravi, Influence of various donors on nonlinear I-V characteristics of tin dioxide ceramics, Appl. Phys. Lett. 83 (2003) 4539–4541.