Electrical Properties of ZPCCT-based Varistor Ceramics

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The microstructure and electrical properties of Zn-Pr-Co-Cr-Tb oxide-based varistors were investigated for different Tb_4O_7 amounts. As the Tb_4O_7 amount increased, the average grain size decreased from 7.7 to 4.8 μm and the sintered density increased from 5.73 to 5.84 g/cm^3. As the Tb_4O_7 amount increased, the varistor voltage increased from 280.9 to 715.8 V/mm and the nonlinear coefficient increased from 26.4 to 44.4. It is assumed that these varistors can be applied for high power with compact size.

Keywords : Microstructure, Tb_4O_7, Electrical properties, Varistors

1. INTRODUCTION

Zinc oxide doped with several different metal oxides is smart eletroceramics showing nonlinear electrical properties, which exhibit abruptly increasing current with increasing voltage. That is, this means the increase of voltage gives rise to the decrease of impedance. This nonlinear of current-voltage properties is because of the presence of a double Schottky barrier (DSB) formed at active grain boundaries containing many trap states. Owing to highly nonlinear properties, these electro-ceramic devices are used widely in the field of overvoltage protection systems from electronic circuits to electric power systems[1,2]. Zinc oxide nonlinear elctroceramics are generally divided into two categories, called Bi_2O_3-based and Pr_6O_{11}-based ceramics, in terms of nonlinear-forming oxides (VFO). ZnO-Bi_2O_3-based ceramics have been mainly studied in different aspects since ZnO non-ohmic ceramics were discovered. Although ZnO-Bi_2O_3-based ceramics show excellent non-ohmic properties, Bi_2O_3 reacts easily with some or many, but not all, of the metals used in preparing multilayer chip nonlinear ceramics, and it destroys the multilayer structure[3]. And it is reported to have an additional insulating spinel phase, which does not play any role in electrical conduction[3]. Recently, ZnO-Pr_6O_{11}-based ceramics have been studied in order to improve a few drawbacks[3] associated with Bi_2O_3[4-14].

Nahm et al. reported that ZnO-Pr_6O_{11}-CoO-Cr_2O_3-REO (REO = Er, Y, Dy, La)-based ceramics have highly nonlinear properties[7-14]. To develop the nonlinear electroceramics of high performance, it is very important to comprehend the effects of the additives on nonlinear properties. The objective of this paper is to investigate the effect of Tb_4O_7 addition on the microstructure and nonlinear properties of ZPCCT (*Z*nO-*P*r_6O_{11}-*C*oO-*C*r_2O_3-*T*b_4O_7)-based ceramics.

2. EXPEIMENTAL PROCEDURE

2.1 Sample preparation

Reagent-grade raw materials were prepared for ZnO varistors with composition (98.0-x) mol% ZnO+0.5 mol% Pr_6O_{11}+1.0 mol% CoO+0.5 mol% Cr_2O_3+x mol% Tb_4O_7 (x = 0.0, 0.25, 0.5, 0.75, 1.0). Raw materials were mixed by ball milling with zirconia balls and acetone in a polypropylene bottle for 24 h. The mixture was dried at 120℃ for 12 h and calcined in air at 750℃ for 2 h. The calcined mixture was pulverized using an agate mortar/pestle and after 2 wt% polyvinyl alcohol (PVA) binder addition, granulated by sieving 200-mesh screen to produce starting powder. The powder was uniaxially pressed into discs of 10 mm in diameter and 2 mm in thickness at a pressure of 800 kg/cm^2. The discs were covered with raw powder in alumina crucible, sintered at 1330℃ for 1 h. The sintered samples were lapped and polished to 1.0 mm thickness. The size of the final samples was about 8 mm in diameter and 1.0 mm in thickness. Silver paste was coated on both faces of samples and ohmic contact of electrodes was formed by heating at 600℃ for 10 min. The electrodes were 5 mm in diameter.

2.2 Microstructure examination

The either surface of samples was lapped and ground with SiC paper and polished with Al_2O_3 powders to a mirror-like surface. The polished samples were thermally etched at 1100℃ for 30 min. The surface microstructure was examined by a scanning electron microscope (SEM, Hitachi S2400, Japan). The average grain size (d) was determined by the lineal intercept method as follows:

$$d = \frac{1.56L}{MN} \quad (1)$$

where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines[15]. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2100, Japan) with CuK_α radiation. The sintered density (ρ) of ceramics was measured by the Archimedes method.

2.3 Electrical measurement

The V-I characteristics of the varistors were measured using a high voltage source measure unit (Keithley 237). The varistor voltage ($V_{1\,mA}$) was measured at a current density of 1.0 mA/cm^2 and the leakage current (I_L) was measured at 0.80 $V_{1\,mA}$. In addition, the nonlinear coefficient (α) was determined from the following expression.

$$\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \quad (2)$$

where J_1 = 1.0 mA/cm^2, J_2 = 10 mA/cm^2, and E_1 and E_2 are the electric fields corresponding to J_1 and J_2, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of ZPCCT-based ceramics for different Tb_4O_7 amounts. The microstructure consisted of primary phase ZnO grain (blackish), and secondary phase intergranular layer (whitish), which

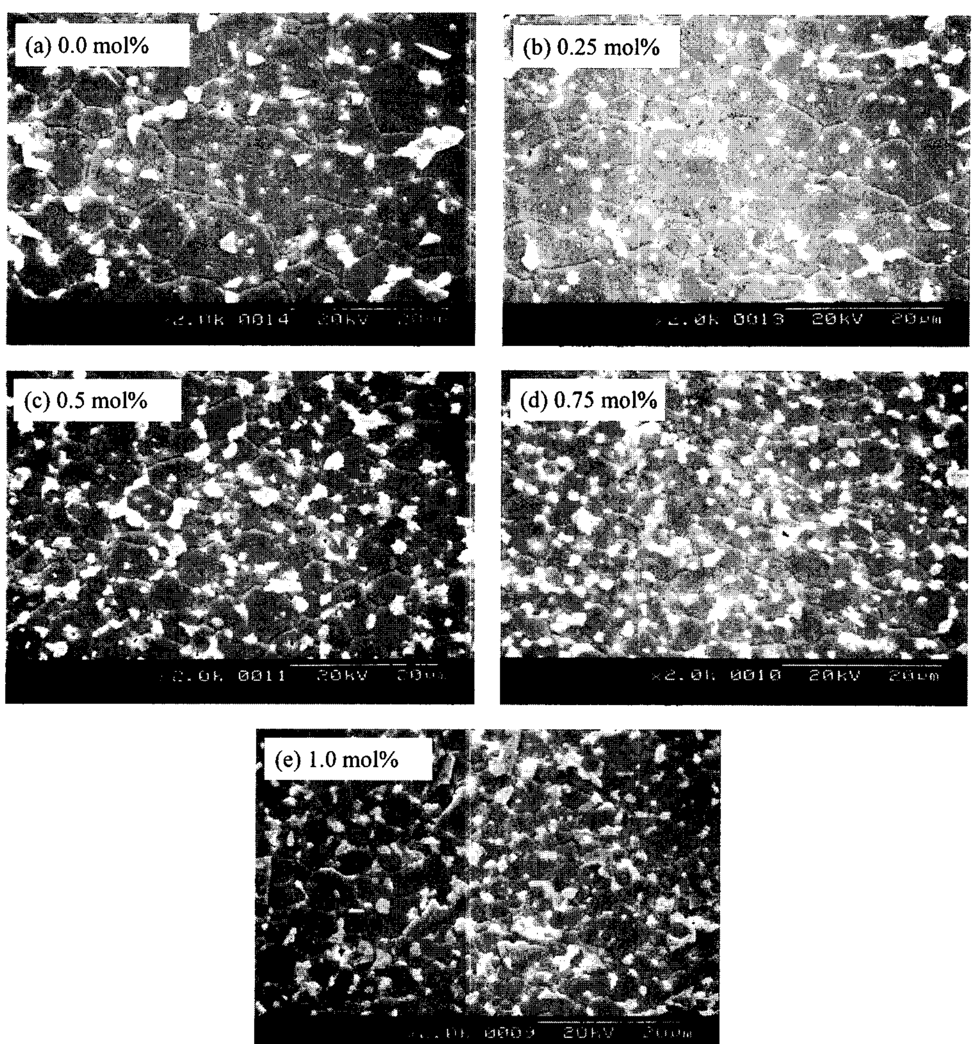

Fig. 1. SEM micrographs of ZPCCT-based varistor ceramics for different Tb_4O_7 amounts.

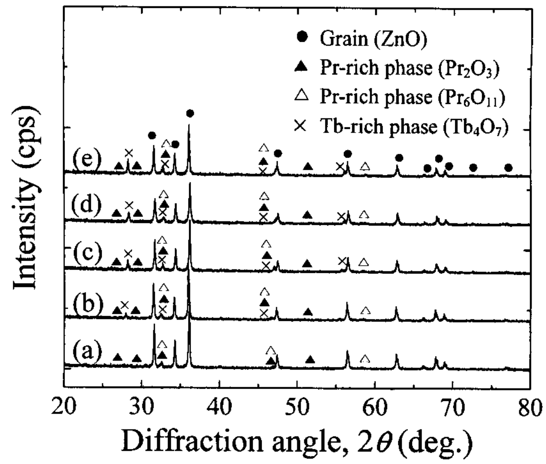

Fig. 2. XRD patterns of ZPCCT-based varistor ceramics for different Tb_4O_7 amounts; (a) 0.0 mol%, (b) 0.25 mol%, (c) 0.5 mol%, (d) 1.0 mol%, and (e) 2.0 mol%.

are Pr- and Tb-rich phases as determined by XRD analysis, as shown in Fig. 2. Fig. 3 shows a distribution of Tb by EDX. No Tb peak into ZnO grain was found within the EDX detection limit. It is assumed that this is attributed to the ionic radius (0.92 Å in Tb) difference for Zn. Added Tb_4O_7 as well as Pr_6O_{11} was segregated to grain boundaries and nodal points, and Pr- and Tb-oxide were found to coexist in the grain boundaries and the nodal points as if they were a single phase.

Figure 4 shows the average grain size and sintered density of the ZPCCT-based ceramics as a function of Tb_4O_7 amount. The sintered density linearly increased in the range of 5.73 to 5.84 g/cm^3 corresponding to 99.1% to 101.0% of TD (5.78 g/cm^3 in ZnO) with the increase of Tb_4O_7 amount. It shows very high density as much as no porosity through the surface microstructure. Nonlinear electroceramics added with a few rare earth oxides (REO) hardly provide both high sintered density and highly nonlinear[9-12]. Therefore, the high sintered density is very important for high energy capability varisors. The average grain size was greatly linearly decreased from 7.7 to 4.8 μm. Therefore, the densification is found to be enhanced by the addition of Tb_4O_7. The detailed microstructure parameters are summarized in Table 1.

Figure 5 shows the *E-J* characteristics of the ZPCCT-based ceramics for different Tb_4O_7 amounts. The curves show the conduction characteristics divide into two regions: linear region before breakdown field and nonlinear region after breakdown field. The sharper the knee of the curves between the two regions, the better the nonlinear properties. On adding more Tb_4O_7, the knee gradually becomes more pronounced and the nonlinear properties are enhanced. Therefore, the addition

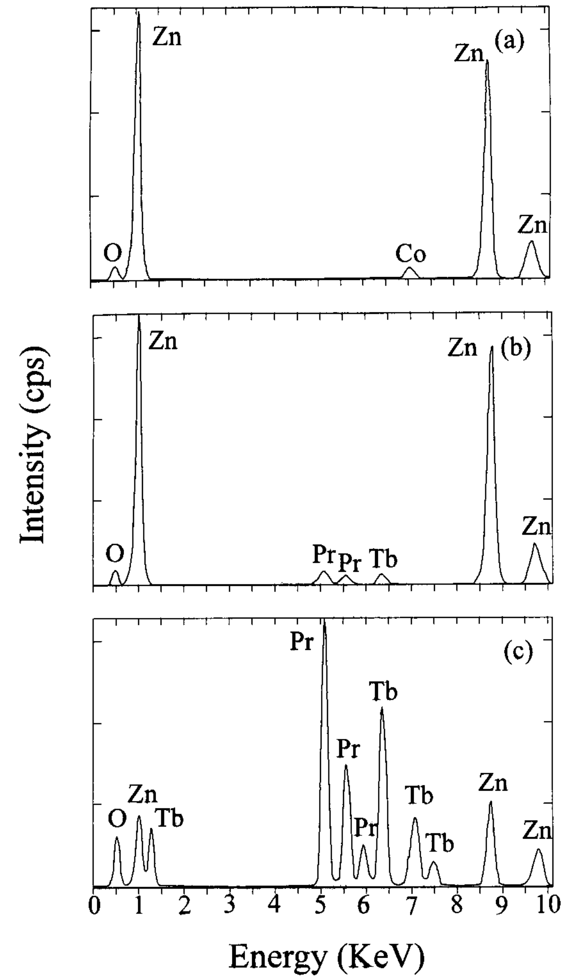

Fig. 3. EDX analysis of ZPCCT-based varistor ceramics for different Tb_4O_7 amounts; (a) ZnO grain, (b) Grain boundary, (c) Intergranular layer.

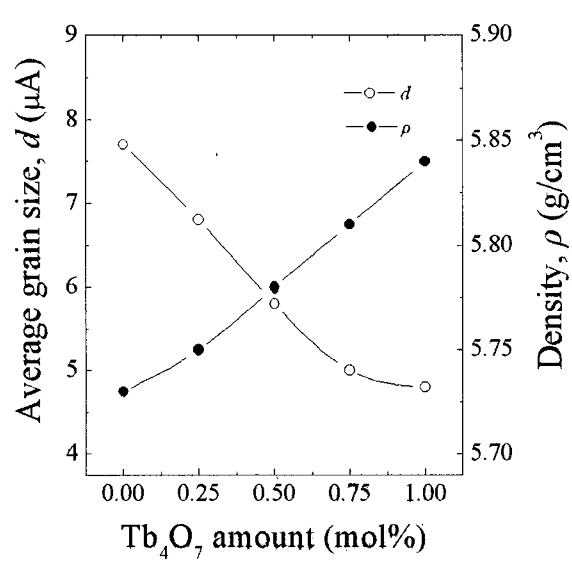

Fig. 4. Average grain size and sintered density as a function of Tb_4O_7 amount.

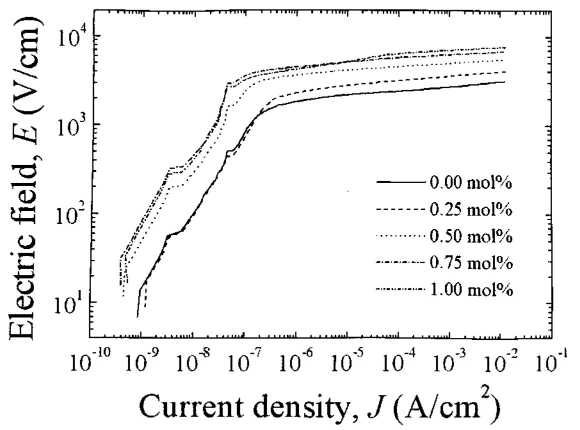

Fig. 5. E-J characteristics of ZPCCT-based varistors for different Tb_4O_7 amounts.

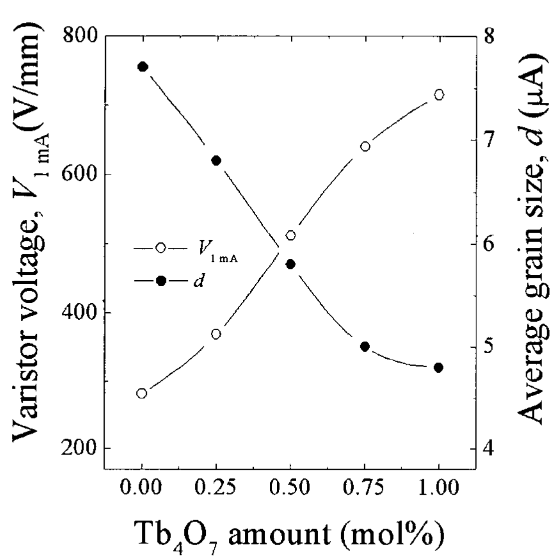

Fig. 6. Varistor voltage and average grain size as a function of Tb_4O_7 amount.

of Tb_4O_7 seems to remarkably enhance nonlinear properties. The varistor voltage ($V_{1\,mA}$) greatly increased from 280.9 to 715.8 V/mm with the increase of Tb_4O_7 amount. The samples added with Tb_4O_7, more than 0.5 mol%, provide a very high varistor voltage of 500 to 700 V/mm per unit thickness. This is very important for high voltage nonlinear ceramics with compact size. The increase of $V_{1\,mA}$ related to Tb_4O_7 amount can be explained by the increase in the number of grain boundaries owing to the decrease in the average ZnO grain size, as shown in Fig. 6. It can be seen that the relation between varistor voltage and average grain size is totally opposite.

Figure 7 shows the variation of the nonlinear coefficient (α) and the leakage current (I_L) of the ZPCCT-based ceramics as a function of Tb_4O_7 amount. The α value of

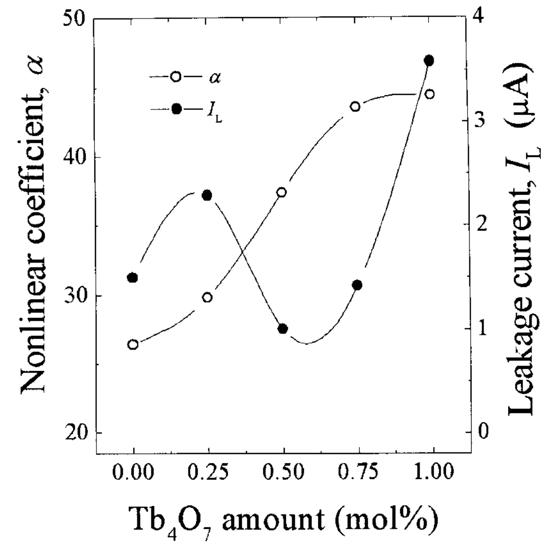

Fig. 7. Nonlinear coefficient and leakage current as a function of Tb_4O_7 amount.

Tb_4O_7-undoped varistors was 26.4 and 0.25 mol% Tb_4O_7-doped varistors slightly increased up to only 29.8 in α value. The varistors doped with Tb_4O_7 more than 0.5 mol% linearly increased in the range of 37.4 to 44.4 with the increase of Tb_4O_7 amount. On the other hand, the I_L value of Tb_4O_7-undoped varistors was only 1.5 μA. When the Tb_4O_7-amount is small, less than 0.25 mol%, the I_L value is higher than that of Tb_4O_7-undoped varistors. As the Tb_4O_7 amount continually increased, the I_L value decreased. When the Tb_4O_7 amount is more than 0.5 mol%, the I_L value decreased again. On the whole, the variation tendency of the I_L value with the increased of Tb_4O_7 amount was very complex unlike α value. Any way, it was found that the addition of Tb_4O_7 to the quaternary system ZnO-Pr_6O_{11}-CoO-Cr_2O_3 improves the nonlinear properties by increasing the nonlinear coefficient.

4. CONCLUSION

The microstructure and electrical properties of varistors were investigated for different Tb_4O_{11} amount. The sintered ceramics increased in the range of 5.73-5.84 g/cm^3 with the increase of Tb_4O_{11} amount. The average grain size decreased from 7.7 to 4.8 μm with the increase of Tb_4O_{11} amount. The nonlinear coefficient increased from 26.4 to 44.4 with the increase of Tb_4O_{11} amount. Conclusively, it is assumed that these varistors can be applied for high power with compact size.

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