Effect of Er_2O_3 Content on Nonlinear Properties and Impulse Clamping Characteristics of Pr/Co/Cr/Al Co-doped Zinc Oxide Ceramics

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ABSTRACT

The microstructure, nonlinear properties, and impulse clamping characteristics of Pr/Co/Cr/Al co-doped zinc oxide ceramics were investigated with various contents of Er_2O_3 . Increasing Er_2O_3 content increased the density of the sintered pellets from 5.69 to 5.83 g/cm³, and decreased the average grain size from 10.6 to 6.5 μm . With increased Er_2O_3 content, the breakdown field increased from 2318 to 4205 V/cm, and the nonlinear coefficient increased from 19.4 to 40.2. The clamp characteristics were improved with the increase of the content of Er_2O_3 . The varistors doped with 2.0 mol% exhibited the best clamp characteristics, in which the clamp voltage ratio was 1.40-1.73 at 1-50 A in an impulse current.

Key words : Microstructure, Erbium, Electrical properties, Electroceramics, Varistors

1. Introduction

Since pure zinc oxide has more zinc atoms than oxygen atoms, it is a nonstoichiometric n-type semiconductor with linear current-voltage behavior under any sintering process. To make it nonlinear, various metal oxides such as bismuth, praseodymium, and barium can be incorporated in the zinc oxide. Sintered zinc oxide ceramics have a distinctive microstructure, in that each of the zinc oxide grains is surrounded by an intergranular layer.^{1,2)} Zinc oxide grains have semiconducting properties, and the intergranular layers are highly resistive. As a result, zinc oxide ceramics exhibit the varistor effect from this distinctive microstructure, which is responsible for the nonlinear property. The nonlinear characteristics are attributed to the double Schottky potential barrier formed at the grain boundary.¹⁻³⁾

Zinc oxide varistors are electronic ceramic devices whose primary function is to sense and limit transient overvoltage. When they are subjected to a voltage above their threshold voltage, zinc oxide varistors act as a conductor, discharging surges to ground. They return to the highly resistive state again when the voltage returns to a normal state. In operation, zinc oxide varistors are devices, which switch from their highly insulating state to highly conducting state with applied voltage, and do so repeatedly without being destroyed. Owing to their high nonlinearity, zinc oxide varistors are widely applied as surge absorbers to protect electronic and electrical systems from transient overvoltage, and surge arresters to protect electric power systems from

lightning surges.^{1,2,4,5)}

Commercial zinc oxide varistor ceramics typically have a ZnO-Bi₂O₃-based composition, which has good nonlinear properties and stability. However, the compound also has a few drawbacks, since Bi₂O₃ is easy to volatilize, and reacts with other oxides at high sintering temperature.⁶⁾ ZnO-PrO₁₁-based ceramics have been studied as new alternative varistor materials to solve the issues of the ZnO-Bi₂O₃-based ceramics.^{4,5,7)} It is well known that Pr/Co co-doped zinc oxide ceramics induce the nonlinear properties in the voltage-current relation.⁸⁻¹⁰⁾ The addition of rare earth oxides can increase the breakdown field and improve the nonlinear coefficient.¹¹⁻¹³⁾ Furthermore, Nahm *et al.* have reported that zinc oxide varistors composed of Zn-Pr-Co-Cr (ZPCC)-R₂O₃ (R = Er, Y, Dy, etc.) exhibited highly nonlinear properties and strong stability.^{12,13)} The Al-doped ZPCCY ceramics had enhanced sinterability despite temperatures as low as 1280°C, and improved stability.¹⁴⁾

In general, quinary system ZPCC-R₂O₃ varistor ceramics are mainly sintered at 1350°C in order to improve sinterability and stability. This sintering temperature is too high, when compared with ZnO-Bi₂O₃-based ceramics. In fact, it is necessary to lower the sintering temperature. So, it is very interesting to explore the combinatory effect of Al₂O₃ and ZPCC-R₂O₃. Furthermore, to develop varistor ceramics for high performance and wide applications, it is important to scrutinize the effects of additives and the sintering process on varistor properties, and their aging behavior against stress.¹⁵⁻²¹⁾ The effect of adding Er_2O_3 on the electrical properties and clamping characteristics of ZPCC-based varistors doped with Al₂O₃ has been not reported. The objective of this work is to investigate the effect of Er_2O_3 on microstructure, nonlinear properties, and impulse clamping characteristics of Pr/Co/Cr/Al co-doped zinc oxide ceramics.

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2. Experimental Procedure

2.1. Sample preparation

The varistor samples were prepared from a blend of (97.995-x) mol% ZnO, 0.5 mol% Pr_6O_{11} , 1.0 mol% CoO, 0.5 mol% Cr_2O_3 , 0.005 mol% Al_2O_3 , x mol% Er_2O_3 , where x ranges from 0 to 2.0. Raw materials were blended by ball-milling with zirconia balls and acetone as a dispersion medium in a polypropylene bottle for 24 h. Each blend was dried at 120°C for 12 h, and calcined in air at 750°C for 2 h. The calcined blend was pulverized using an agate mortar and pestle, and after 2 wt% polyvinyl alcohol (PVA) binder addition, granulated by sieving through a 100-mesh screen to produce the starting powder. The powder was pressed into disk-shaped pellets of 10 mm diameter and 2 mm thickness at a pressure of 100 MPa. The pellets were sintered at 1300°C for 3 h, and furnace-cooled to room temperature. The heating and cooling rates were 4°C/min. The sintered pellets were lapped and polished to 1.0 mm thickness using a lapping/polishing machine (GLP-S20/25; GLP Korea, Geumchun-Gu, Seoul, Korea). The final samples were about 8 mm diameter and 1.0 mm thickness. Silver paste was painted on both faces of the samples, and the electrodes were formed by heating it at 550°C for 10 min. The electrodes were 5 mm in diameter. Finally, the lead wire was soldered on both electrodes, and the samples were packaged by dipping them into a thermoplastic resin powder.

2.2. Microstructure examination

One side of the sintered pellets was lapped and ground with SiC paper, and then polished with 0.3 μm - Al_2O_3 powders to a mirror-like surface. The polished samples were thermally etched at 1050°C for 20 min. The surface microstructure was examined by using a field emission electron microscope (FESEM, Quanta 200, FEI, Brno, Czech). The average grain size d was determined through the lineal intercept method using the expression, $d = 1.56 L/MN$, where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of grain boundaries intercepted by the lines.²²⁾ A compositional analysis was carried out for the minor phases using an energy dispersion X-ray spectroscopy (EDS) attached to the SEM unit. The crystalline phases were identified by using an X-ray diffractometry (XRD, X'pert-PRO MPD, Panalytical, Almelo, Netherlands) with CuK_α radiation. The sintered density ρ of the pellets was measured by using a density determination kit (238490) attached to a balance (AG 245, Mettler Toledo International Inc., Greifensee, Switzerland), with deionized water as a liquid medium.

2.3. Electrical measurement

The electric field-current density (E-J) characteristics were measured by using a high voltage source-measure unit (Keithley 237, Keithley Instruments Inc., Cleveland, OH, USA). The breakdown field E_B was measured at 1.0 mA/cm^2 and the leakage current density J_L was measured at 0.8 E_B .

In addition, the nonlinear coefficient α is defined by the empirical law, $J = K \cdot E^\alpha$, where J is the current density, E is the applied electric field, and K is a constant. α_1 at the low current region was calculated through the expression,¹⁾ $\alpha_1 = (\log J_2 - \log J_1) / (\log E_2 - \log E_1)$, where $J_1 = 1.0 \text{ mA}/\text{cm}^2$ and $J_2 = 10 \text{ mA}/\text{cm}^2$, E_1 and E_2 are the electric fields corresponding to J_1 and J_2 , respectively.

2.4. Clamping voltage measurement

The clamping voltage V_c was measured at impulse-currents I_p of 1, 5, 10, and 25 A using a surge generator (Tae-yang Engineering, Busan, Korea) and an oscilloscope (TeK 3020B, Beaverton, Oregon, USA). The impulse current waveform had a width of 20 μs and a rise time of 8 μs ($8 \times 20 \mu\text{s}$). The clamp voltage ratio $K = V_c / V_{1 \text{ mA}}$ is defined by the ratio of clamping voltage to breakdown voltage. The breakdown voltage $V_{1 \text{ mA}}$ was measured at 1.0 mA DC. The nonlinear coefficient α_2 at the high current region was calculated through the expression, $\alpha_2 = (\log I_{p2} - \log I_{p1}) / (\log V_{c2} - \log V_{c1})$, where $I_{p1} = 1.0 \text{ A}$, $I_{p2} = 10 \text{ A}$, and V_{c1} and V_{c2} are the clamping voltages corresponding to I_{p1} and I_{p2} , respectively.

3. Results and Discussion

Figure 1 shows the crystal structure from XRD patterns of the samples with various contents of Er_2O_3 . Outwardly, the microstructure of the samples consist of phases such as ZnO grain bulk as a primary phase, and Pr- and Er-rich phases as minor secondary phases.¹²⁾ The phases generated by the reaction between additives were nowhere to be found within the detection limit of the XRD.

Figure 2 shows SEM micrographs of the varistor samples with various contents of Er_2O_3 . Secondary Pr- and Er-rich phases were found to exist at mainly triple grain junctions, partial grain boundaries, and occasionally within the grains. It can be seen that the amount of secondary phases increased with increasing content of Er_2O_3 . It is believed

Fig. 1. XRD patterns of the samples with various contents of Er_2O_3 : (a) 0.0 mol%, (b) 0.25 mol%, (c) 0.5 mol%, (d) 1.0 mol%, and (e) 2.0 mol%.

Fig. 2. SEM micrographs of the samples with various contents of Er_2O_3 : (a) 0.0 mol%, (b) 0.25 mol%, (c) 0.5 mol%, (d) 1.0 mol%, and (e) 2.0 mol%.

Fig. 3. EDS analysis of the varistor sample: (a) ZnO grain, (b) Grain boundary, and (c) Nodal point.

that this is attributed to Er segregation due to the large ionic radius of Er when compared with Zn. The ingredient of the secondary phase is confirmed through the EDS analysis in Fig. 3. It is a mixed phase composed of Pr and Er, as if they were a single phase.

The changing tendency of the average grain size d as a function of the content of Er_2O_3 is indicated graphically in Fig. 4(a). The average grain size d increased to a small extent from 9.6 to 10.6 μm up to 0.25 mol% content of Er_2O_3 . However a further Er_2O_3 increase caused the average grain size d to decrease to 6.5 μm at 2.0 mol%. On the whole, the decrease of average grain size d is attributed to the fact that the movement of the grain boundaries is hindered by the increasing amount of secondary phase due to Er_2O_3 segrega-

tion at the grain boundaries. As a result, Er_2O_3 acted as a grain growth inhibitor when the content of Er_2O_3 exceeded 0.25 mol%.

The changing tendency of the density ρ of the sintered pellets as a function of the content of Er_2O_3 is indicated graphically in Fig. 4(b). The density ρ of the sintered pellets increased significantly from 5.69 to 5.83 g/cm^3 (5.78 g/cm^3 in pure ZnO) with increasing content of Er_2O_3 . It was found that Er_2O_3 doping makes a denser ceramic matrix, with almost no porosity. The sinterability of this system was noticeably improved with the densification and uniformity of grain, sintering at 1300°C, as compared with ZnO- Pr_6O_{11} -based ceramics sintered at 1350°C, with no Al_2O_3 .¹²⁾ This showed the obvious effect of Al_2O_3 additives. The detailed microstructure parameters are summarized in Table 1.

Figure 5 shows the E-J characteristics of the samples with various contents of Er_2O_3 . The E-J relation features a voltage-switching curve: an OFF state below threshold voltage, and an ON state over threshold voltage. The OFF state reveals an extremely high resistance as a linear E-J relation, and the ON state reveals an extremely low resistance as a nonlinear E-J relation.

The changing tendency of the breakdown field E_B as a function of the content of Er_2O_3 is presented graphically in Fig. 4(c). The breakdown field E_B decreased to a small extent from 2318 to 2194 V/cm up to 0.25 mol% content of Er_2O_3 . However a further increase caused the breakdown field E_B to increase to 4205 V/cm at 2.0 mol%. The behavior of E_B in accordance with the content of Er_2O_3 can be explained through the expression, $E_B = v_{gb}/d$, where d is the average grain size and v_{gb} is the breakdown voltage per grain boundaries. This expression indicates that the E_B is directly determined by d and v_{gb} . In general, the increase of E_B results from the increase in the number of grain bound-

Table 1. Average Grain Zize (d), Sintered Density (ρ), Breakdown Field (E_B), Breakdown Voltage Per Grain Boundary (v_{gb}), Nonlinear Coefficient (α_1), and Leakage Current Density (J_L) of the Samples with Various Contents of Er_2O_3

Er_2O_3 content (mol%)	d (μm)	ρ (g/cm^3)	E_B (V/cm)	v_{gb} (V/gb)	α_1	J_L ($\mu\text{A}/\text{cm}^2$)
0.0	9.6	5.69	2318	2.2	19.4	93.2
0.25	10.6	5.72	2194	2.3	28.0	21.4
0.5	9.0	5.73	2482	2.2	35.6	11.6
1.0	8.0	5.76	2764	2.2	28.9	30.3
2.0	6.5	5.83	4205	2.7	40.2	17.8

Fig. 4. Microstructure and electrical parameters as a function of the contents of Er_2O_3 : (a) average grain size (d), (b) sintered density (ρ), (c) breakdown field (E_B), (d) nonlinear coefficient (α_1), and (e) leakage current density (J_L). **Fig. 5.** E-J characteristics of the samples with various contents of Er_2O_3 : (a) 0.0 mol%, (b) 0.25 mol%, (c) 0.5 mol%, (d) 1.0 mol%, and (e) 2.0 mol%.

aries due to the decrease of the average ZnO grain size.

The changing tendency of the nonlinear coefficient α_1 as a function of the content of Er_2O_3 is shown graphically in Fig. 4(d). On the whole, the nonlinear coefficient α_1

increased from 19.4 to 40.2 with increasing content of Er_2O_3 . However, the nonlinear coefficient α_1 exhibited a fluctuation at 0.25 mol%. Obviously, it can be seen that Er_2O_3 doping has an effect on the nonlinear properties of these ceramics based on α behavior. In light of the changing tendency of α_1 , Er_2O_3 doping is understood to affect the density of interface states at the grain boundaries, and subsequently, affect the Schottky barrier height according to the variation of the electronic states.

The changing tendency of the leakage current density J_L as a function of the content of Er_2O_3 is illustrated graphically in Fig. 4(e). The leakage current density J_L decreased to a large extent from 93.2 to 11.6 $\mu\text{A}/\text{cm}^2$ with increasing content of Er_2O_3 . However, the leakage current density J_L increased to 30.3 $\mu\text{A}/\text{cm}^2$ again at 1.0 mol%. On the whole, Er_2O_3 doping was found to decrease the leakage current density J_L . Furthermore, the leakage current of these varistor samples exhibited high values when compared with other $\text{ZnO-Pr}_6\text{O}_{11}$ varistors.¹²⁻¹⁴ The high leakage current density J_L seems to be related to the combinatory effect of Al_2O_3 and Er_2O_3 , although it is not clear at present.

Figure 6 shows the impulse current I_p waveforms of 50 A

Fig. 6. Clamping voltage waveform for impulse current (50 A) of the samples with various contents of Er_2O_3 : (a) 0.0 mol%, (b) 0.25 mol%, (c) 0.5 mol%, (d) 1.0 mol%, and (e) 2.0 mol%.

and clamping voltage V_c waveform of the samples with various contents of Er_2O_3 . The threshold voltage at the low current (mA unit) region is called the varistor voltage (breakdown voltage), and is dominated by grain boundaries. The clamping voltage V_c is determined by measuring the voltage between terminals of the sample when the specified impulse current flows through the sample, and is dominated by grain resistance. Therefore, clamping voltage is not equal to varistor voltage. Clamping voltage varies with the magnitude of the impulse current because of the finite resistance of the varistor itself, and increases with increasing impulse current. In addition, high breakdown voltage leads to high clamping voltage, as indicated in Fig. 6.

The closer the clamping voltage is to the varistor voltage, the better the clamping characteristics. Therefore, clamp voltage ratio K is much more important than clamping voltage in varistors. The effect of Er_2O_3 doping on clamp voltage

Fig. 7. Clamp voltage ratio and nonlinear coefficient (α_2) as a function of the contents of Er_2O_3 .

ratio K is indicated in Fig. 7. On the whole, clamp voltage ratio K increased with increasing impulse current for the specified content of Er_2O_3 due to the increase of clamping voltage V_c . The clamp voltage ratio K decreased with increasing content of Er_2O_3 for the specified impulse current. This means that the changing tendency of nonlinear coefficient α_1 coincides with that of nonlinear coefficient α_2 , with increasing content of Er_2O_3 . In other words, the nonlinear coefficient α_1 increased with increasing content of Er_2O_3 , as mentioned previously, and the nonlinear coefficient α_2 increased from 12.9 to 19.7 with increasing content of Er_2O_3 , as indicated in Fig. 7. However, this tendency is not always applied to all varistor systems.

The detailed data for clamping voltage V_c and clamp voltage ratio K values of the samples corresponding to an impulse current of 1–50 A, with various contents of Er_2O_3 are summarized in Table 2. Among the samples, those doped with 2.0 mol% content Er_2O_3 exhibited the best clamp characteristics by exhibiting the lowest clamp voltage ratio K ($K = 1.40$ – 1.73) for an impulse current of 1–50 A. It can be seen that the appropriate content of Er_2O_3 can improve the clamp voltage ratio K .

4. Conclusions

This study investigated how Er_2O_3 content has an effect on the microstructure, nonlinear properties, and impulse clamping characteristics of Pr/Co/Cr/Al co-doped zinc oxide

Table 2. Nonlinear Coefficient (α_2), Clamping Voltage and Clamp Voltage Ratio of the Samples with Various Contents of Er_2O_3 .

Er_2O_3 content (mol%)	α_2	$V_{1\text{mA}}$ (V)	V_c (V)					$K = V_c/V_{1\text{mA}}$				
			$I_p = 1$ A	5A	10A	25A	50A	$I_p = 1$ A	5A	10A	25A	50A
0.0	14.4	253.0	392	440	460	492	529	1.55	1.74	1.82	1.94	2.09
0.25	12.9	232.8	360	408	430	460	490	1.55	1.75	1.85	1.98	2.10
0.5	14.3	260.0	402	452	472	508	536	1.55	1.74	1.82	1.95	2.06
1.0	15.0	293.0	446	496	520	552	584	1.52	1.69	1.77	1.88	1.99
2.0	19.7	438.7	614	668	690	726	760	1.40	1.52	1.57	1.65	1.73

ceramics. These ceramics showed a microstructure consisting of bulk grain and a kind of secondary phase. Increasing content of Er_2O_3 increased the density of sintered pellets due to the incorporated Al_2O_3 , unlike ZPCCE ceramics, and these ceramics exhibited a high sintered density despite sintering at 1300°C . Otherwise, increasing the content of Er_2O_3 decreased the average grain size. With increased Er_2O_3 content, the breakdown field increased, and the nonlinear coefficient was improved. Increasing the content of Er_2O_3 improved clamp characteristics, and the varistor doped with 2.0 mol% exhibited a good clamp voltage ratio of 1.73 at 50 A in an impulse current.

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