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Microstructure, electrical and dielectric properties, and aging behavior of ZPCCA varistor ceramics with Er_2O_3 doping

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Abstract: The microstructure, electrical and dielectric properties, and DC-accelerated aging of the ZPCCA (ZnO-Pr_6O_{11}-CoO-Cr_2O_3-Al_2O_3) ceramics were investigated with various contents of Er_2O_3. The ceramic phases consisted of a bulk phase of ZnO grains, and a minor secondary phase of mixture of Pr_6O_{11} and Er_2O_3. The increase of the content of doped Er_2O_3 increased the densities of sintered pellet from 5.66 to 5.85 g/cm^3, and decreased the average grain size from 9.6 to 6.3 μm. With the increase of the content of doped Er_2O_3, the breakdown field increased from 2390 to 4530 V/cm, and the nonlinear coefficient increased from 28.4 to 39.1. The sample doped with 0.25 mol.% Er_2O_3 exhibited the strongest electrical stability; variation rates for the breakdown field measured at 1.0 mA/cm^2, and for the non-ohmic coefficient were –3.4% and –23.8%, respectively, after application of a stress of 0.95 E_B/125 °C/24 h.

Keywords: microstructure; Er_2O_3; electrical properties; aging behavior; varistor ceramics; rare earths

Zinc oxide is so-called *n*-type semiconductor of wide band gap (ab. 3.2 eV) or so-called II-VI defect oxide semiconductor because of a nonstoichiometric defect structure that the zinc ion is more than oxygen ion. So far, zinc oxide must be the most suitable materials, among varistor materials, in the light of commercial goods or researching field. Pure zinc oxide ceramics will be revealed ohmicity in the voltage-current relation. However, impurity doped zinc oxide ceramics will be revealed nonohmicty, due to electrostatic potential barrier at grain boundary by sintering. This is called just varistor effect. Therefore, zinc oxide varistors are a kind of polycrystalline ceramics with highly nonlinear voltage-current characteristics. Zinc oxide varistors are fabricated by sintering zinc oxide pellets doped with primary additives such as Bi_2O_3, Pr_6O_{11} and V_2O_5, and secondary additives such as CoO, Sb_2O_3, MnO, Cr_2O_3, etc.[1–3].

Zinc oxide varistors are very similar to back-to-back zener diode in the voltage-current relation. They are the same as insulating properties below a threshold voltage, and highly nonlinear properties above a threshold voltage[1–3]. As a result, zinc oxide varistor acts as a switching device by sensing transient overvoltage coming from electrical environment before and after application of critical voltage. Therefore, zinc oxide varistors are usefully utilized as a core element of surge absorbers to protect electronic and electrical circuits from overvoltage, and as a core element of surge arrester to protect electric power systems from lightning surge[1–5].

Commercial zinc oxide varistors are based on Bi-based ceramics and Pr-based ceramics in terms of varistor-forming oxides inducing varistor's inherent property. Bi-based zinc oxide varistors are the most powerful varistors for low, medium, and high voltage since varistor's discovery, and still have been studied with additives and sintering process[6–8]. Pr-based zinc oxide varistors are mainly used to multilayered chip varistors (MLV) based on high stability, and occasionally used to power facilities[4,5]. The biggest merits of Pr-based zinc oxide varistors are microstructurally simple, and electrically good nonlinear properties and stability[4,9–22]. However, the biggest demerits are expensive Pr oxide and high sintering temperature.

Nahm et al. reported that the rare earth oxides improved nonlinear properties and stability against various stress in zinc oxide varistors composed of Zn-Pr-Co-Cr (ZPCC)-R_2O_3 (R=Er, Y, Dy, etc.)[13–18]. Really, the microstructure and electrical properties of zinc oxide varistor ceramics can be modified by the addition of various metal oxides[19–24]. The small content of Al_2O_3 enhanced the sinterability even at temperature as low as 1280 ºC as well as the strong stability against a stress in the quinary system ZPCCY[17,18]. In order to improve varistor characteristics or process technology, it is very interesting to scrutinize the roles and combinatory effect of the additives. The effect of Er_2O_3 doping on the electrical properties of the ZPCC-based varistors added with Al_2O_3 has little been reported. The aim of this work was to investigate the effect of Er_2O_3 doping on the microstructure, electrical and dielectric properties, and DC-accelerated

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aging behavior of the quinary system ZPCCA.

1 Experimental

1.1 Sample preparation

The composition of the varistor samples was as follows: (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 (all reagent-grade, x=0.0, 0.25, 0.5, 1.0, and 2.0). Raw materials were mixed with zirconia balls and acetone in a polypropylene bottle for 24 h using a ball mill. The mixture was dried at 120 ºC for 12 h and calcined in air at 750 ºC for 2 h. The calcined mixture was mixed with acetone and polyvinyl alcohol binder (2.0 wt.% based on powder weight) in a beaker using a magnetic stirring bar. The powder pulverized using an agate mortar and pestle was granulated by sieving through a 100-mesh screen to produce the starting powder. The powder was uniaxially pressed into disk-shaped pellets of 10 mm diameter and 2 mm thickness at a pressure of 100 MPa. The pellets were sintered for 2 h at 1300 ºC and furnace-cooled to room temperature. The heating and cooling rates were 4 ºC/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 of about 8 mm diameter and 1.0 mm thickness. Silver paste was coated on both faces of the varistor samples and the electrodes were formed by heating it at 550 ºC for 10 min. The electrodes were 5 mm in diameter. Finally, the lead wire was soldered to both electrodes, and the samples were packaged by dipping them into a thermoplastic resin powder.

1.2 Microstructure analysis

Both surfaces of the sintered pellets were 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 ºC for 20 min. The surface microstructure was examined by a scanning 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 the grain boundaries intercepted by the lines[25]. The compositional analysis for minor phases was carried out by an energy dispersion X-ray spectroscope (EDS) attached to the SEM unit. The crystalline phases were identified by X-ray diffractometry (XRD, X′pert-PRO MPD, Panalytical, Almelo, Netherlands) with Cu Kα radiation. The densities ρ of sintered pellets were measured 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.

1.3 *E-J* characteristics measurement

The electric field-current density (E-J) characteristics were measured 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 was calculated through the expression[1–3], α=(lgJ_2-lgJ_1)/(lgE_2-lgE_1), where J_1=1.0 mA/cm^2, J_2=10 mA/cm^2, E_1 and E_2 are the electric fields corresponding to J_1 and J_2, respectively.

1.4 Dielectric characteristics measurement

The dielectric characteristics, such as the apparent dielectric constant (ε_{APP}') and dissipation factor (tanδ) of the samples were measured at the range of 100 Hz–2 MHz using an RLC meter (QuadTech 7600, Marlborough, MA, USA).

1.5 DC-accelerated aging characteristics measurement

The DC-accelerated aging stress test was performed under four continuous conditions as follows: the first stress: 0.85 E_B/115 ºC/24 h, the second stress: 0.90 E_B/120 ºC/24 h, and the third stress: 0.95 E_B/125 ºC/24 h. The leakage current was recorded at intervals of 1 min during applying the stress using a high voltage source-measure unit (Keithley 237). After application of a stress, the E-J characteristics were measured at room temperature.

2 Results and discussion

2.1 Effect of sintering on microstructure

Fig. 1 shows XRD patterns of the varistor samples with various contents of Er_2O_3. Outwardly, the microstructure of the varistor samples consisted of ZnO grain bulk as a primary phase, and Pr-rich and Er-rich phase as minor secondary phases[13]. Er-rich phase detected when the content of doped Er_2O_3 was 1.0 mol.%, whereas the reaction phase related to Er was not detected within detection limit of XRD. It is well known that Pr-based zinc oxide ceramics has a simple microstructure[4,9,11,12].

Fig. 2 shows SEM micrographs of the varistor samples with various contents of Er_2O_3. The secondary phase was found to exist at mainly nodal points, next grain boundaries, and occasionally within the grains. Furthermore, the amount of secondary phases increased obviously with the increase of the content of doped Er_2O_3. The EDS analysis in Fig. 3 shows that the secondary phase at the grain,