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Zinc oxide-praseodymia semiconducting varistors having a powerful surge suppression capability

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ABSTRACT

We introduced the varistor having more powerful surge suppression capability. This research focuses on the effect of sintering time on electrical properties and pulse current degradation of Pr/Co/Cr/Y/Mg co-doped zinc oxide varistors for surge suppression. With increasing sintering time, the breakdown field decreased from 2768 to 1680 V/cm, and the nonlinear coefficient decreased from 57.7 to 29.3. Considering pulse current, a higher nonlinear coefficient led to the lower clamp voltage ratio. Therefore, the sample sintered for 1 h exhibited the best clamp characteristics, in which the clamp voltage ratio was in the range of K = 1.52–1.77 for pulse currents of 1–10 A and K = 2.04–3.43 for pulse currents of 400–2500 A. Considering pulse absorption capability, the sample sintered for 3 h exhibited the strongest electrical stability; −3.9% in $\Delta E_{1\ mA/cm^2}$ / $E_{1\ mA/cm^2}$ and −6.9% $\Delta\alpha_1$ / α_1 after application of a pulse current of 2500 A.

1. Introduction

It is well known that varistor is core component in SPD or surge arrester. It is no exaggeration to say that varistor performance determines system reliability. Varistor is a nonlinear resistor, in which the current flow linearly until the applied voltage reaches the breakdown voltage, whereas the current increase abruptly when the applied voltage exceeded the breakdown voltage [1–3].

Presently, the majority of zinc oxide varistors are firstly doped with bismuth, which inherently induces the nonlinearity. They are widely applied based on excellent electrical properties and stable aging characteristics. However, they have a few flaws coming from a special relation between bismuth and sintering temperature: the volatility of bismuth and a lot of secondary phases by high sintering temperature [4]. Nowadays, power facilities connected with IT system demand the SPD or surge arrester, which exhibits the high stability and reliability. We think that zinc oxide varistors doped with praseodymium are an alternative to currently fabricated ZnO–Bi_2O_3-based varistors [5,6]. The work on this system has been begun in earnest since the early 1990s [5–9], and has been known to yield a high varistor effect and the stability against various stresses [10–16]. Researchers are more interested in the varistors having stable characteristics against a pulse current stress considering system reliability [17,18]. On the whole, a few zinc oxide varistors doped with praseodymium were tested under a high pulse current stress, unlike a lot of zinc oxide varistors doped with bismuth. As published, zinc oxide varistors doped with erbium, zinc oxide varistors doped with yttrium, and zinc oxide varistors doped with dysprosium were tested under a pulse current of 1200 A [19–21]. They exhibited good performance under a pulse current stress, based on commercial specification.

Basically, improvement of a surge suppression capability and clamp voltage ratio is related to the grain resistance. Above all, the grain resistance should be firstly decreased in order to restrict an ohmic loss by joule heat at high current. Therefore, it is necessary to add donor impurities, which decrease the grain resistance to further improve surge characteristics [21,22]. It is known that aluminum has a role as a donor for the decrease of grain resistance [23]. On the other hand, the increase of electron concentration in the conduction band is possible by sintering process, without impurity addition [13]. There are no published reported studying the effect of sintering time on the clamping characteristics and the degradation behavior under a big pulse current of 2500 A.

In this study, the effect of sintering time on electrical properties and pulse current degradation of Pr/Co/Cr/Y/Mg co-doped zinc oxide varistors was systematically investigated, and the effect of MgO addition was partially discussed, when compared with zinc oxide varistors doped with yttrium [20]. The Pr/Co/Cr/Y/Mg co-doped zinc oxide varistors exhibited more powerful surge suppression capability than any varistors reported until now.

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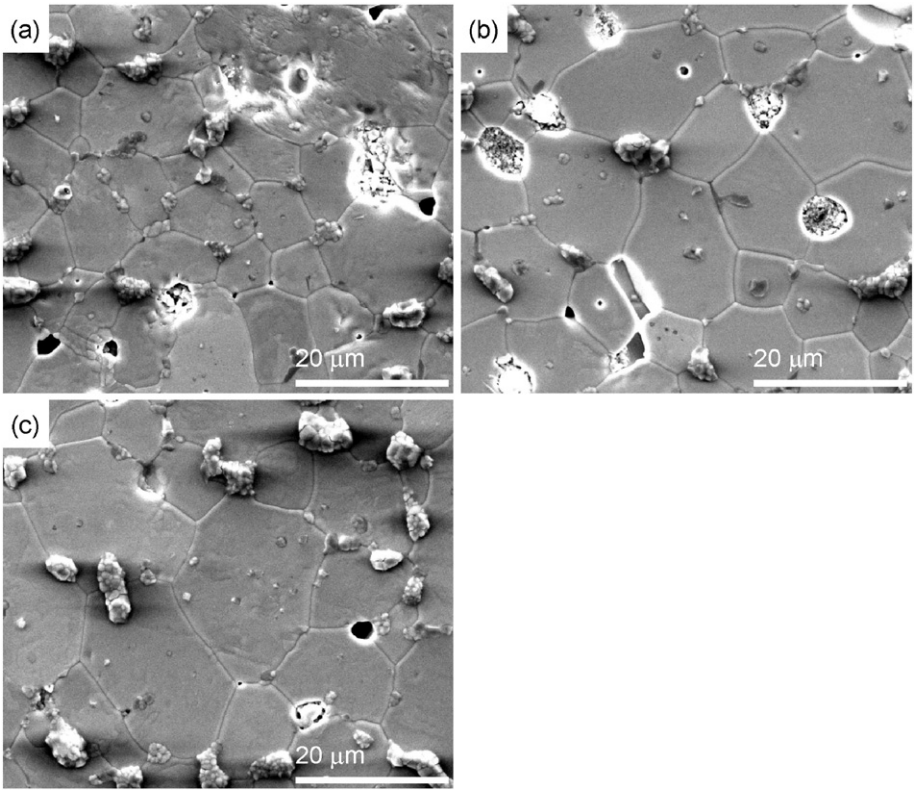

Fig. 1. SEM micrographs of the samples with different sintering times; (a) 1 h, (b) 2 h, and (c) 3 h.

2. Experimental procedure

2.1. Sample preparation

Reagent-grade raw materials (purity of 99.9%) composed of 97.4 mol% ZnO + 0.5 mol% $PrO_{1.83}$ + 1.0 mol% CoO + 0.5 mol% Cr_2O_3 + 0.5 mol% Y_2O_3 + 0.1 mol% MgO were utilized. The accuracy of weighed amounts was ±0.1 mg. The raw materials were blended with zirconia balls and acetone as the dispersion medium in a polypropylene bottle for 24 h using a ball mill. The slurry blend was dried at 120 °C for 12 h and calcined in air at 750 °C for 2 h. The calcined blend was blended with ionized water and polyvinyl alcohol (2 wt.% based on powder weight) in a beaker using a magnetic stirring bar. After drying at 120 °C for 24 h, the blend was pulverized using an agate mortar/pestle, and granulated by sieving through a 100-mesh screen to produce the starting powder. The granulated powder was uniaxially pressed into disk-shaped pellets of 10 mm in diameter and 2.0 mm in thickness under a pressure of 100 MPa. The pellets were sintered for different times (1, 2, 3 h) at 1350 °C and furnace-cooled to room temperature. The heating and cooling rates were 4 °C/min, respectively. The sintered pellets were lapped and polished. The final pellets were 8 mm in diameter and 1.4 mm in thickness, using a lapping/polishing machine (GLP-S20/25; GLP Korea, Geumchun-Gu, Seoul, Korea). Conductive silver paste was coated on both faces of the pellet and the electrodes were formed by heating it at 550 °C for 10 min. The electrodes were 5 mm in diameter. Finally, lead wire was soldered to both electrodes, and the samples were packaged by dipping them into a thermoplastic resin powder.

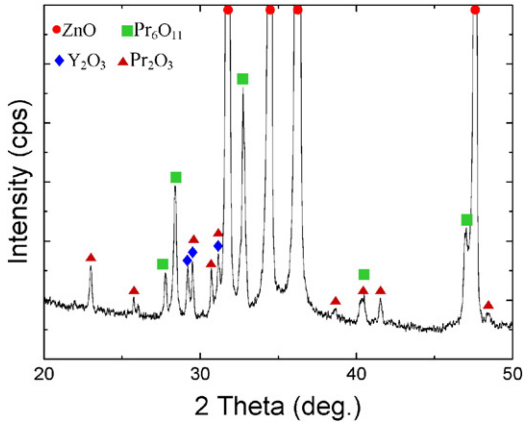

Fig. 2. XRD patterns of the sample.

2.2. Microstructure analysis and measurements

For microstructure characterization, one surface of pellets was lapped and ground with SiC paper and polished with 0.3 μm-Al powder to a mirror-like surface. The polished pellets were thermally etched at 1050 °C for 30 min. The surface microstructure was examined by a scanning electron microscope (FESEM, Quanta 200, FEI, Brno, Czech). The average grain size (d) was determined by 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]. The compositional analysis for minor phases was carried out by energy dispersion X-ray spectroscopy (EDS) attached to the SEM unit. The crystalline phases were identified by X-ray diffractometry (XRD, X′pert-PRO MPD, Panalytical, Almelo, Netherlands) with CuK_α 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).

2.3. Electrical measurements

The electric field–current density (E–J) characteristics were measured using a high voltage source-measure unit (Keithley 237, Keithley