Microstructure and nonlinear electrical properties of ZnO-Pr_6O_{11}-CoO-Cr_2O_3-La_2O_3-based varistors

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Published online: 16 September 2005

ZnO varistors are attractive ceramic semiconductor devices made by sintering ZnO powder with minor additives, such as Bi_2O_3, Pr_6O_{11}, CoO, and so on. Each ZnO grain acts as if it is has a semiconductor junction at the grain boundary. Since nonlinear electrical behavior occurs at each boundary the varistors can be considered as a multijunction device composed of many series and parallel connection of grain boundaries. The grain size distribution plays a major role in electrical behavior.

ZnO varistors exhibit highly nonlinear voltage–current (V–I) characteristics because of the electronic phenomena occurring near the grain boundaries. In other words, they act as an insulator below the varistor voltage, called the breakdown voltage, and a conductor thereafter. Moreover, they possess excellent surge withstanding capability. They, therefore, have been widely utilized as the surge absorbers in electronic systems and the core elements of surge arresters in electric power systems [1, 2]. Many researchers wish to fabricate ZnO varistors with a higher nonlinearity. The majority of commercial varistors are Bi_2O_3-based ZnO varistors containing Bi_2O_3, which inherently induces nonlinear properties. Recently, Pr_6O_{11}-based ZnO varistors 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-based varistors have highly nonlinear properties when rare-earth metal oxides, R_2O_3 (R = Er, Y, Dy) are used [6–14]. This paper reports on ZnO-Pr_6O_{11}-CoO-Cr_2O_3-La_2O_3 (in short ZPCCL)-based varistors which exhibit excellent nonlinearity.

Reagent-grade raw materials were used in proportions of $(98.0 - x)$ mol% ZnO, 0.5 mol% Pr_6O_{11}, 1.0 mol% CoO, 0.5 mol% Cr_2O_3, x mol% La_2O_3 (where $x = 0.0$–2.0). The mixture was calcined in air at 750 °C for 2 hr. The calcined powders were pressed into discs 10 mm in diameter and 2 mm in thickness at a pressure of 80 MPa. The discs were sintered at 1300 °C in air for 1 hr. 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 the samples and ohmic contacts were formed by heating at 600 °C for 10 min. The electrodes were 5 mm in diameter.

The surface microstructure was examined by scanning electron microscopy (SEM, Model S2400, Hitachi, Japan). The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2100, Japan) with CuK_α radiation. The compositional analysis of the selected areas was determined by an attached energy dispersion X-ray analysis (EDX) system. The average grain size (d) of the varistor ceramics was determined by the linear intercept method [15]. The sintered density (ρ) was measured by the Archimedes method. The V–I characteristics of the varistors were measured using a Keithley 237 unit. 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 exponent (α) was determined from $\alpha = 1/(\log E_2 - \log E_1)$, where E_1 and E_2 are the electric fields corresponding to 1.0 and 10 mA/cm^2, respectively.

Fig. 1 shows the SEM micrographs of ZPCCL-based ceramics with various La_2O_3 contents. It is well known that the microstructure of Pr_6O_{11}-based ZnO varistor ceramics consist of only two phases [4]: ZnO grain (bulk phase) and intergranular layer (second phase). The intergranular layers in ZPCCL-based ceramics were Pr- and La-rich phases as determined by XRD analysis, as shown in Fig. 2. As can be seen in the figure, three diffraction peaks were revealed in the ZPCL-based ceramics, namely, ZnO grains, Pr oxides, and La oxide. It was found from EDX that these coexist at the grain boundaries and the nodal points as if they were a single phase. No La peak was found in the ZnO grain within the EDX detection limit (Fig. 3). It was observed by SEM that as the La_2O_3 content increases, the intergranular phase gradually becomes more concentrated at the nodal points. These microstructures are not greatly different from varistor ceramics doped with Er, Y, and Dy, as reported previously [6, 9, 14]. As the La_2O_3 content increases, the density increased from 4.71 to 5.77 g/cm^3 for 1.0 mol%, with further additions did not affecting density, which saturated at 5.77 g/cm^3. The average grain size increases from 4.0 to 8.5 μm with increasing La_2O_3 content due to precipitation of Pr_6O_{11} and La_2O_3 at grain boundaries. The detailed microstructual parameters are summarized in Table I.

Fig. 4 shows the E–J characteristics of the ZPCCL-based varistors with various La_2O_3 contents. The varistors show conduction characteristics dividing into two regions: pre-breakdown at low field and breakdown at high field. The sharper the knee of the curve between the two regions, the better the nonlinearity. It can be forecasted that the 0.5 mol% La_2O_3-doped varistor should exhibit the best nonlinear properties because

0022-2461
DOI: 10.1007/s10853-005-4567-y

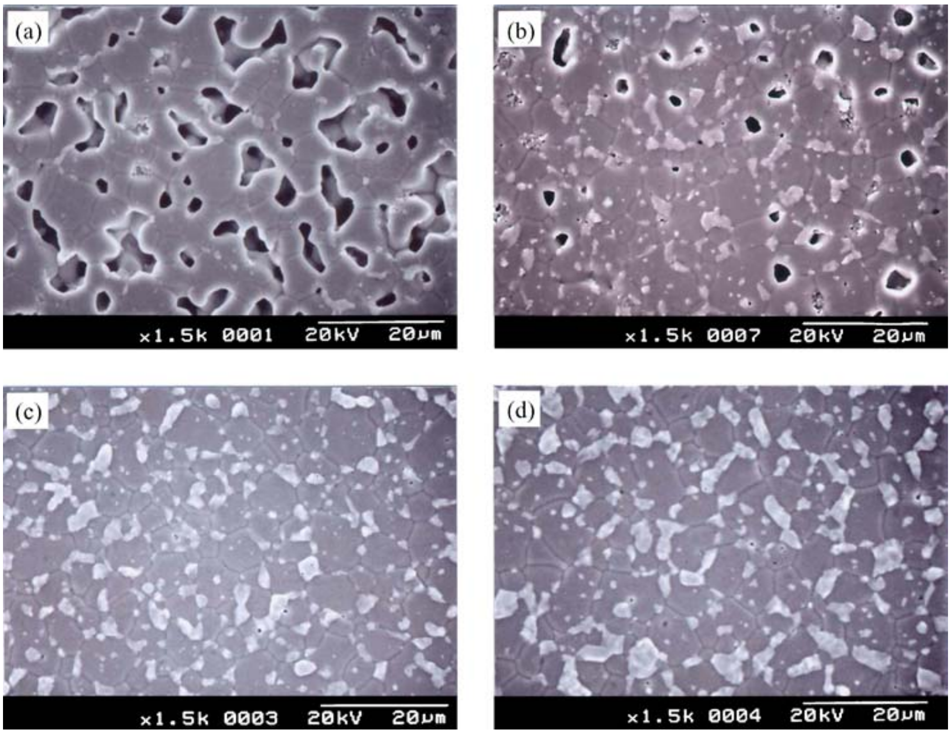

Figure 1 SEM micrographs of ZPCCL-based ceramics with various La_2O_3 contents: (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%.

TABLE I Microstrucrural and V–I characteristic parameters of ZPCCL-based varistors with various La_2O_3 contents

La_2O_3 content (mol%)	ρ (g/cm^3)	d (μm)	V_{1mA} (V/mm)	V_{gb} (V/gb)	α	I_L (μA)
0.0	4.71	4.0	503.5	2.0	63.0	2.1
0.5	5.40	6.9	427.2	2.9	81.6	0.2
1.0	5.77	7.9	108.0	0.8	7.1	50.6
2.0	5.77	8.5	9.4	0.08	3.1	100.2

Theoretical density (ρ) of $ZnO = 5.78$ g/cm^3

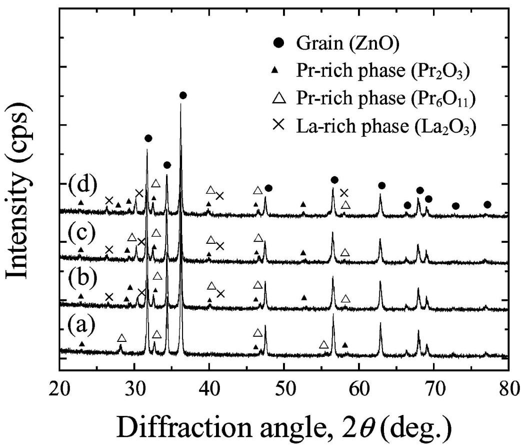

Figure 2 XRD patterns of ZPCCL-based ceramics with various La_2O_3 contents: (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%.

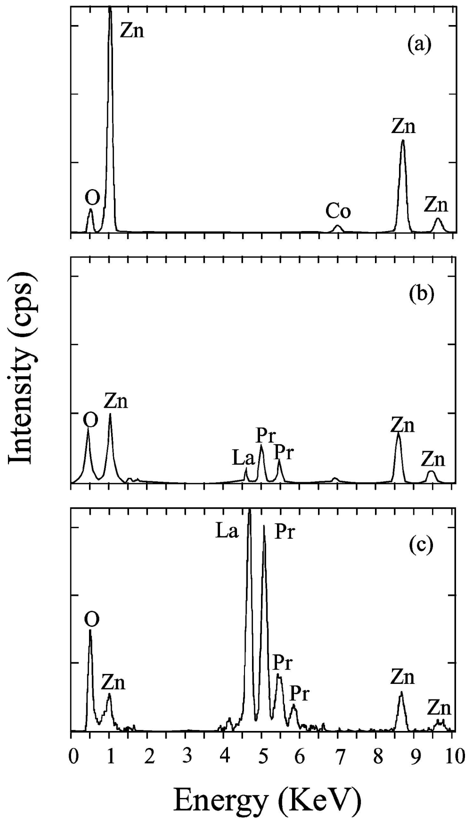

Figure 3 EDX analysis of ZPCCL-based ceramics with 0.5 mol% La_2O_3 content; (a) ZnO grain, (b) grain boundary, and (c) intergranular layer.

it has the sharpest knee. On adding more La_2O_3, the knee gradually becomes less pronounced and the nonlinear properties reduce. The detailed V–I characteristic parameters are summarized in Table I. The varistor voltage ($V_{1\,mA}$) decreased abruptly from 503.5 to 9.4 V/mm as the La_2O_3 content increased. This is attributed firstly to the decrease in the number of grain boundaries caused by the increase in the ZnO grain size, and secondly, to the abrupt decrease of varistor voltage per grain boundary (V_{gb}). The varistors doped with La_2O_3 exceeding 0.5 mol% exhibited much lower V_{gb} values than the general values of 2–3 V/gb. These

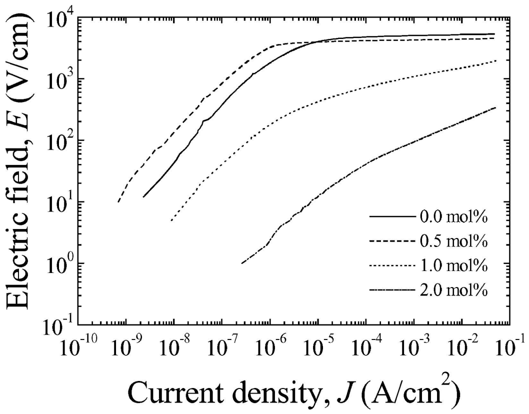

Figure 4 *E–J* characteristics of ZPCCL-based varistors with various La_2O_3 contents.

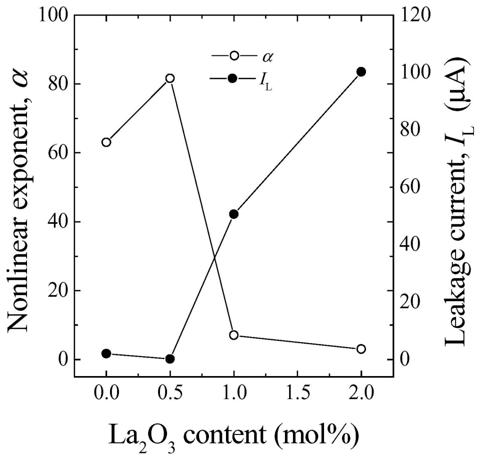

Figure 5 Variation of nonlinear exponent and leakage current of ZPCCL-based varistors as a function of La_2O_3 contents.

varistors will exhibit very poor nonlinear properties presumably.

Fig. 5 shows the variation of the nonlinear exponent (α) and the leakage current (I_L) as a function of La_2O_3 content. The α value was calculated to be 63.0 for the sample without La_2O_3. This value was much higher than values for the quaternary system ZnO-Bi_2O_3-CoO-Cr_2O_3, which never exceeded 25 [16]. As the La_2O_3 content increases, the α value increased, achieving a maximum value (81.6) for the sample with 0.5 mol% La_2O_3. This represents excellent nonlinearity, which cannot be easily obtained in ZnO varistors. This is the highest value in Pr_6O_{11}-based ZnO varistors of five components that has been achieved. Increasing additive content further to 2.0 mol% caused the α value to decrease. On the other hand, as the La_2O_3 content increases, the I_L value decreased, achieving a minimum value (0.2 μA) for the sample with 0.5 mol% La_2O_3. Increasing the additive content further to 2.0 mol% caused the I_L value to increase significantly. It can be seen that the variation of I_L shows the inverse relationship to the variation of α with La_2O_3 content. Therefore, it is clear that the nonlinear properties are strongly influenced by the incorporation of La_2O_3.

In summary, a moderate La_2O_3 content, in the vicinity of 0.5 mol%, can greatly improve the nonlinear properties of quaternary system ZnO-Pr_6O_{11}-CoO-Cr_2O_3-based varistors.

Acknowledgments

This work was supported by the ECC (Electronic Ceramics Center) at Dongeui University as RRC. TIC program through KOSEF (Korea Science and Engineering Foundation), ITEP (Korea Institute of Industrial Technology Evaluation and Planning), and Busan Metropolitan City.

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Received 26 July 2004
and accepted 6 May 2005