# $La_2O_3$ Addition Influence on Electrical Characteristics of $Pr_6O_{11}$-based ZnO Varistors

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The microstructure and electrical properties of the varistors, which are composed of ZnO-$Pr_6O_{11}$-CoO-$Cr_2O_3$-$La_2O_3$-based ceramics, were investigated for different $La_2O_3$ contents. The increase of $La_2O_3$ content led to more densified ceramics, whereas abruptly decreased the nonlinear properties by incorporating beyond 1.0 mol%. The highest nonlinearity was obtained from 0.5 mol% $La_2O_3$, with the nonlinear coefficient of 81.6 and the leakage current of 0.2 μA. The increase of sintering time and temperature greatly decreased the nonlinear properties. As the $La_2O_3$ content increased, the donor density increased from $0.64 \times 10^{18}$ /cm$^3$ to $16.89 \times 10^{18}$ /cm$^3$ and the barrier height greatly decreased with increasing $La_2O_3$ content, reaching a maximum (1.47 eV) in 0.5 mol% $La_2O_3$.

*Keywords* : Microstructure, Electrical properties, Varistors, $Pr_6O_{11}$, $La_2O_3$

## 1. INTRODUCTION

Zinc oxide (ZnO) is *n*-type oxide-semiconductor of nonstoichiometric defect structure that the zinc ion is more than oxygen ion. So, this is usefully used as material applying to gas sensor, devices using grain boundary effect, and so on. ZnO varistors are solid-state electronic devices manufactured by sintering a semi-conducting ZnO grains with minor additives, such as $Bi_2O_3$, CoO, $Cr_2O_3$, and so on. ZnO varistors exhibit highly nonlinear conduction characteristics. In other words, ZnO varistors act as an insulator below the breakdown voltage, called the breakdown voltage, and a conductor thereafter. Moreover, ZnO varistors possess excellent surge withstanding capability. Therefore, they have been widely applied to surge protection device (SPD) such as the surge absorbers in electronic systems and the surge arresters in electric power systems[1,2].

Their electrical characteristics are related to a unit structure composed of ZnO grain-intergranular layer-ZnO grain in the bulk of the devices. A unit structure acts as if it is has a semiconductor junction at grain boundary. Since the nonlinear electrical behavior occurs at a boundary of each semiconducting ZnO grain, the varistors can be considered a multi-junction device composed of many series and parallel connection of grain boundary. The grain size distribution plays a major rule in electrical behavior.

Many researchers who are interested in the varistors commonly wish to fabricate the ZnO varistors having 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 are actively being studied in order to improve a few drawbacks[3] due to the high volatility and reactivity of $Bi_2O_3$[4-11]. Nahm et al. reported that ZnO-$Pr_6O_{11}$-based varistors have high nonlinear properties by incorporating of rare-earth metal oxides[7-11].

This paper is to investigate the effect of $La_2O_3$ on microstructure, nonlinear properties, and capacitance-voltage characteristics of $Pr_6O_1$-based ZnO varistors.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Sample preparation

Reagent-grade raw materials were prepared for ZnO varistors with composition (98.5-x) mol% ZnO, 0.5 mol% $Pr_6O_{11}$, 0.5 mol% CoO, 0.5 mol% $Cr_2O_3$, x mol% $La_2O_3$ (x = 0.0-2.0). 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 two fixed sintering temperature 1300 ℃ and 1340 ℃ for 1 h. The heating rate and cooling rate were 4 ℃/min. 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 0.3 μm-$Al_2O_3$ powder 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 such as the following equation[12].

$$d = \frac{1.56L}{MN} \tag{1}$$

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. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2100, Japan) with $CuK_\alpha$ radiation. The density ($\rho$) 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 breakdown 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 ($\alpha$) was determined from the following equation[13].

$$\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \tag{2}$$

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.

The capacitance-voltage ($C$-$V$) characteristics of varistors were measured at 1 kHz using a RLC meter (QuadTech 7600) and an electrometer (Keithley 617). The donor density ($N_d$) and the barrier height ($\phi_b$) were determined by the following equation[14].

$$\left(\frac{1}{C_b} - \frac{1}{2C_{bo}}\right)^2 = \frac{2(\phi_b + V_{gb})}{q\varepsilon N_d} \tag{3}$$

where $C_b$ is the capacitance per unit area of a grain boundary, $C_{bo}$ is the value of $C_b$ when $V_{gb}$ = 0, $V_{gb}$ is the applied voltage per grain boundary, $q$ is the electronic charge, $\varepsilon$ is the permittivity of ZnO ($\varepsilon$ = 8.5$\varepsilon_o$). The density of interface states ($N_t$) at the grain boundary was determined by the following equation[14].

$$N_t = \left(\frac{2\varepsilon N_d \phi_b}{q}\right)^{1/2} \tag{4}$$

Once the donor density and barrier height are known, the depletion layer width ($t$) of either side at the grain boundaries was determined by the following equation [15].

$$N_d\, t = N_t \tag{5}$$

## 3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs with various $La_2O_3$ contents of varistors sintered at 1300 ℃. It is well known that the microstructure of $Pr_6O_{11}$-based ZnO varistors is consisted of only two phases[16]: ZnO grain (bulk phase) and intergranular layer (second phase). The intergranular layers in varistors were Pr- and La-rich phases by XRD analysis, as shown in Fig. 2. As can be seen in the Figure, three diffraction peaks were revealed in varistors, namely, ZnO grains, Pr oxides, and $La_2O_3$ oxide. It was observed by SEM that as the $La_2O_3$ content increased, the intergranular phase gradually more distributed at the grain boundaries and particularly the nodal points. It is believed that this is attributed to the segregation of La toward grain boundaries due to the difference of ionic radius. These microstructures are not greatly different with varistors doped with Er, Y, and Dy, as reported previously[7,9,11]. As the $La_2O_3$ content increased, the density increased from 4.71 to 5.77 g/cm$^3$ up to 1.0 mol%, whereas the further addition did not affect density, which saturated at 5.77 g/cm$^3$. The average grain size increased 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. Though the increase of $La_2O_3$ content increased $La_2O_3$ segregation at the grain boundaries, the average grain size increased with increasing $La_2O_3$ content. In the light of increasing of density and grain size for increasing $La_2O_3$ segregation,

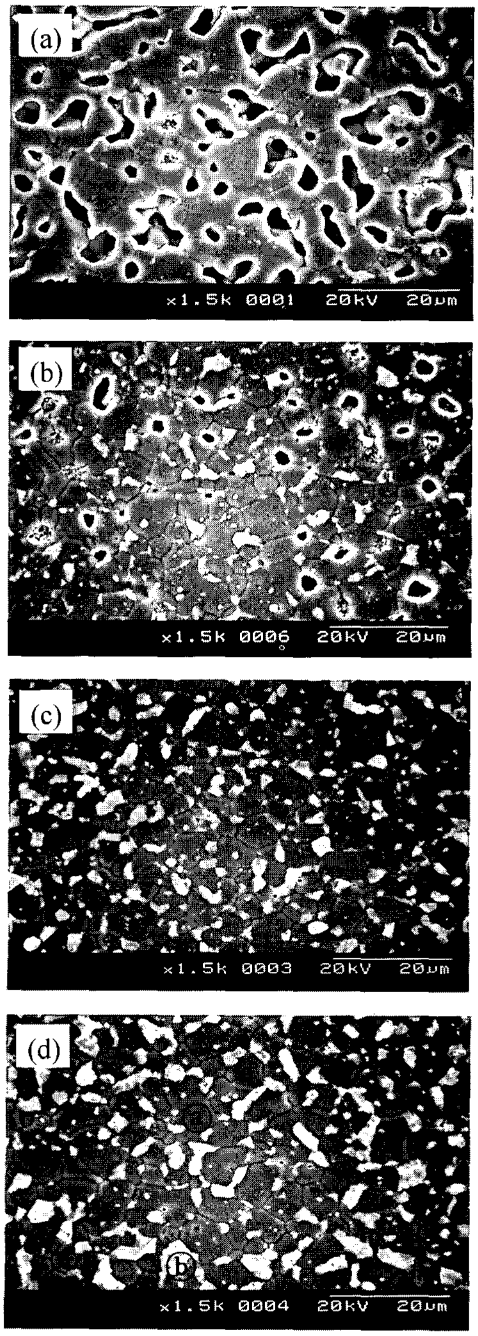


Fig. 1. SEM micrographs with various $La_2O_3$ contents of varistors sintered at 1300 ℃; (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%(ⓐ: ZnO grain and ⓑ: intregranular layer).

$La_2O_3$ seems to severe as an adder related to liquid phase sintering.

The tendency of increase in the average grain size directly affects the breakdown voltage in the electrical properties. The detailed microstructual parameters are summarized in Table 1.

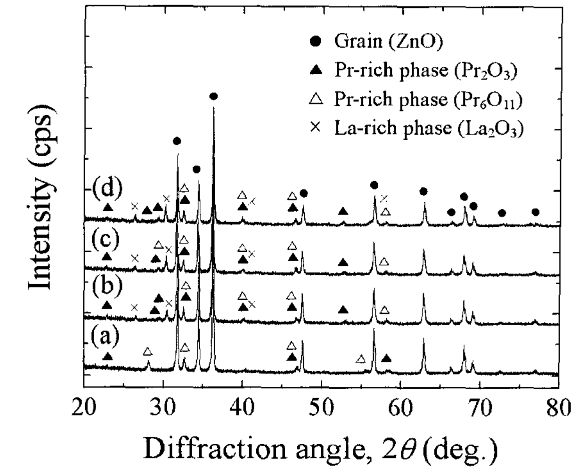


Fig. 2. XRD patterns with various $La_2O_3$ contents of varistors sintered at 1300 ℃; (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%.

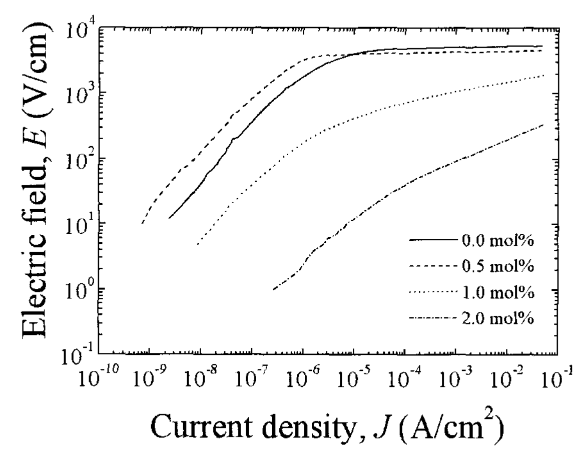


Fig. 3. *E-J* characteristics with various $La_2O_3$ contents of varistors sintered at 1300℃.

Figure 3 shows the *E-J* characteristics with various $La_2O_3$ contents of varistors sintered at 1300 ℃. The conduction characteristics of varistors are divided into two regions: pre-breakdown at low field and breakdown at high field.

The sharper the knee of the curves between the two regions, the better the nonlinearity. It can be forecasted that the varistors doped with 0.5 mol% $La_2O_3$ would exhibit the best nonlinear properties because of the sharpest knee. 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 1. The breakdown voltage ($V_{1mA}$) decreased abruptly from 503.5 to 9.4 V/mm as the $La_2O_3$ content increased. This is attributed firstly to the decrease

Table 1. Microstructural and *V-I* characteristic parameters with various $La_2O_3$ contents of varistors sintered at 1300 ℃ for 1 h.

| $La_2O_3$ content (mol%) | $\rho$ (g/cm$^3$) | $d$ (μm) | $V_{1\,mA}$ (V/mm) | $V_{gb}$ (V/gb) | $\alpha$ | $I_L$ (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 |

in the number of grain boundaries caused by the increase in the ZnO grain size, and secondly, to the abrupt decrease of breakdown voltage per grain boundaries ($V_{gb}$). The varistors doped with $La_2O_3$ exceeding 0.5 mol% exhibited much lower $V_{gb}$ value than general value of 2-3 V/gb. These varistors will exhibit very poor nonlinear properties presumably. The breakdown voltage per grain boundaries ($V_{gb}$) is defined by the following equation.

$$V_{gb} = (\frac{d}{D})V_{1\,mA} \quad (6)$$

where $d$ is the average grain size and $D$ is thickness of sample.

The nonlinear coefficient ($\alpha$) value was calculated to be 63 in the case of undoped varistors. This value was much higher than that of Zn-Bi-Co-Cr-based ceramics, which never exceed 25[13]. As the $La_2O_3$ content increased, the $\alpha$ value increased, achieving a maximum value (81.6) for varistors with 0.5 mol% $La_2O_3$. This value is easily unobtainable excellent nonlinearity in ZnO varistors. This is the highest value in $Pr_6O_{11}$-based ZnO varistors of 5-components reported until now. Increasing $La_2O_3$ content further to 2.0 mol% caused the $\alpha$ value (3.1) to decrease. On the other hand, as the $La_2O_3$ content increased, the leakage current ($I_L$) value decreased, achieving a minimum value (0.2 μA) for varistors with 0.5 mol% $La_2O_3$. Increasing $La_2O_3$ content further to 2.0 mol% caused the $I_L$ value (100.2 μA) to increase extremely. It can be seen that the variation of $I_L$ shows the inverse relationship to the variation of $\alpha$ with $La_2O_3$ content. As a result, it is clear that the nonlinear properties are strongly influenced by the incorporation of $La_2O_3$. The reason why 0.5 mol% $La_2O_3$ exhibits the highest nonlinearity is attributed to the highest barrier height, which will be referred in *C-V* characteristics. When the varistor doped with 0.5 mol% $La_2O_3$ was sintered at 1300 ℃ for 2 h, the *V-I* charteristic parameters are summarized in Table 2.

Table 2. *V-I* characteristic parameters of 0.5 mol% $La_2O_3$-doped varistors sintered at 1300 ℃ for 2 h.

| $La_2O_3$ content (mol%) | $\rho$ (g/cm$^3$) | $d$ (μm) | $V_{1\,mA}$ (V/mm) | $V_{gb}$ (V/gb) | $\alpha$ | $I_L$ (μA) |
|---|---|---|---|---|---|---|
| 0.5 | 5.42 | 7.50 | 395.5 | 2.9 | 45.1 | 0.3 |

Table 3. *V-I* characteristic parameters with various $La_2O_3$ contents for varistors sintered at 1340 ℃.

| $La_2O_3$ content (mol%) | $V_{1\,mA}$ (V/mm) | $\alpha$ | $I_L$ (mA/cm$^2$) |
|---|---|---|---|
| 0.0 | 130.4 | 12.0 | 0.03 |
| 0.5 | 14.4 | 2.4 | 0.13 |
| 1.0 | 13.5 | 4.2 | 0.08 |
| 2.0 | 9.6 | 5.0 | 0.07 |

The increase of sintering time does not affect sintered density, whereas it gives rise to the decrease of breakdown voltage ($V_{1\,mA}$), in particular, the nonlinear coefficient ($\alpha$) greatly decreased in approximately half of $\alpha$ value in varistors sintered at 1300 ℃ for 1 h.

On the other hand, the increase of sintering temperature greatly affected the conduction characteristics. The *V-I* charaterstic parameters for varistors sintered at 1340 ℃ are summarized in Table 3. The breakdown voltage ($V_{1mA}$) greatly decreased in the range of 130.4 to 9.6 V/mm, compared with those of varistors sintered at 1300 ℃. 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 breakdown voltage per grain boundaries ($V_{gb}$), as mentioned previously. Furthermore, the increase of sintering temperature greatly deteriorated the nonlinear properties. As $La_2O_3$ content increased, the $\alpha$ value increased unlike varistors sintered at 1300 ℃. The $La_2O_3$ addition rather decreased the nonlinear properties, by exhibiting the $\alpha$ value less than 5. This show the selection of sintering temperature in manufacturing process is very important.

Figure 4 shows *C-V* characteristics with various $La_2O_3$ contents of varistors sintered at 1300 ℃. The detailed characteristic parameters are summarized in Table 4.

The $N_d$ value increased abruptly monotonously in the range of $0.64\text{x}10^{18}$-$16.89\text{x}10^{18}$ /cm$^3$ with increasing $La_2O_3$ content. This means the $La_2O_3$ acts as a donor.

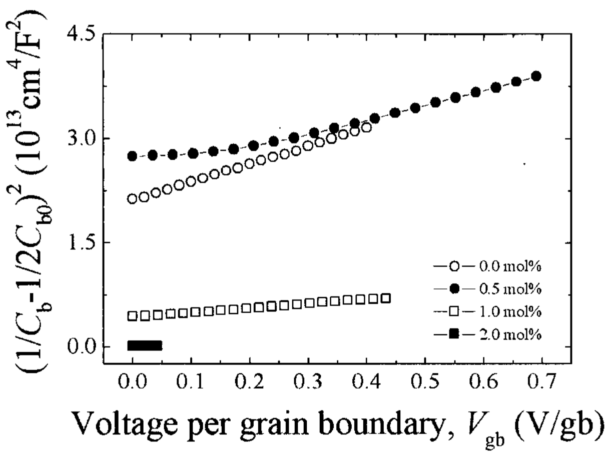


Fig. 4. *C-V* characteristics with various $La_2O_3$ contents for varistors sintered at 1300 ℃.

Table 4. *C-V* characteristic parameters with various $La_2O_3$ contents for varistors sintered at 1300 ℃.

| $La_2O_3$ content (mol%) | $N_d$ ($10^{18}/cm^3$) | $N_t$ ($10^{12}/cm^2$) | $\phi_b$ (eV) | $t$ (nm) |
|---|---|---|---|---|
| 0.0 | 0.64 | 2.21 | 0.82 | 34.6 |
| 0.5 | 0.94 | 3.60 | 1.47 | 38.4 |
| 1.0 | 2.59 | 4.04 | 0.67 | 15.6 |
| 2.0 | 16.89 | 5.16 | 0.17 | 3.1 |

Although $La^{3+}$ ions have a larger radius (0.106 nm) than $Zn^{2+}$ ions (0.074 nm), limited substitution within the ZnO grains is possible. La substitutes for Zn and creates lattice defect in ZnO grains. The chemical-defect reaction using Kroger-Vink notation can be written as the following equation.

$$La_2O_3 \xrightarrow{ZnO} 2La^{\cdot}_{Zn} + 3O^{\times}_{O} + 2e' \quad (7)$$

where $La^{\cdot}_{Zn}$ is a positively charged La ion substituted for Zn lattice site and $O^{\times}_{O}$ is a neutral oxygen of oxygen lattice site. The electron generated in reaction above increases the donor density. The $t$ value on either side of depletion region decreased in the range of $t$ = 34.6-3.1 nm with increasing $La_2O_3$ content.

This shows opposite relation to the $N_d$. In general, the depletion region extends farther into the side with a lighter doping. On the other hand, the increase of $La_2O_3$ content led to the increase in the $N_t$ value in the range of $2.21\times10^{12}$-$5.16\times10^{12}/cm^2$. The $\phi_b$ value decreased in the range of 1.4-0.17 eV with increasing $La_2O_3$ content, reaching a maximum (1.47 eV) in 0.5 mol% $La_2O_3$. This coincides with the variation of $\alpha$ value in *V-I* characteristics. The $\phi_b$ is directly associated with the $N_d$ and $N_t$. In other words, the $\phi_b$ is estimated by the variation rate in the $N_t$ and $N_d$. In general, the $\phi_b$ is increased with increasing $N_t$ and decreasing $N_d$.

## 4. CONCLUSION

The microstructure and electrical properties of varistors were investigated with various $La_2O_3$ contents. The ceramics were more densified in the range of 4.71-5.77 $g/cm^3$ with increasing $La_2O_3$ content. The breakdown voltage decreased abruptly in the range of 503.5 to 9.4 V/mm with increasing $La_2O_3$ content. It was found that a moderate $La_2O_3$ content, in the vicinity of 0.5 mol%, could greatly improve the nonlinear properties of quaternary system ZnO-$Pr_6O_{11}$-CoO-$Cr_2O_3$-based varistors. The varistors with 0.5 mol% $La_2O_3$ exhibited excellent nonlinear properties, which the nonlinear coefficient is 81.6 and the leakage current is 0.2 μA. The $La_2O_3$ was additive acting as a donor by increasing donor density with increasing $La_2O_3$ content. On the other hand, the nonlinear properties of varistors sintered at 1340 ℃ greatly decreased by marking less than 5 in nonlinear coefficient. The barrier height at grain boundary was less than 1 eV for all $La_2O_3$ addition, except for 0.5 mol% $La_2O_3$ with 1.4 eV.


## ACKNOWLEDGEMENTS

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