Sintering Behavior and Electrical Properties of ZnO–PbO Ceramics

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ZnO–PbO セラミックスの焼結挙動と電気的性質

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ZnO doped with PbO in the range of 0.5 to 5 mol% was sintered at temperatures of 1273 to 1573 K, and microstructure and current-voltage characteristics were examined. Liquid Pb-rich Pb–Zn–O phase was penetrated among ZnO grains during sintering of ZnO–PbO composites, forming a grainboundary layer. However, PbO addition prevented densification during sintering due to the high vapor pressure of liquid PbO. The current-voltage behavior of the ZnO–PbO composites was non-linear. The resistivity of the ZnO–PbO composites decreased with increasing sintering temperature and approached that of pure ZnO. The non-linear coefficient of the ZnO–PbO composites is small, and hardly depends on the PbO content and the sintering temperature.

[Received January 31, 2002; Accepted June 18, 2002]

Key-words: ZnO, PbO, Varistor, Sintering behavior, Microstructure, Electrical properties

1. Introduction

Zinc oxide varistors doped with several oxides have widely been applied for ceramic electronic devices as voltage limiters and surge protectors due to highly non-ohmic current-voltage (I – V) characteristics.^{1,2)} Their electrical properties, especially nonlinear coefficient, are improved by the addition of oxides of Bi, Sb, Co, Mn, etc. Of various additives, Bi₂O₃^{3)–5)} and Pr₆O₁₁^{6),7)} form grain boundary phases in ZnO varistors, and primarily cause the non-ohmic I – V behavior. Bi₂O₃ and Pr₆O₁₁ have the common properties in phase relations with ZnO:^{4),7)} liquid phases are formed at low temperatures by eutectic reactions; dopant oxide phases (Pr₂O₃ and β -Bi₂O₃ + δ -Bi₂O₃) precipitate after cooling; the dopant oxides dissolve hardly into solid ZnO phase. The other oxides have subsidiary effects such as varying electrical conductivity and improving non-linearity and sinterability. Although cobalt and manganese oxides have no effect on the non-linearity of ZnO, they considerably increase that of ZnO–Bi₂O₃.^{3),8),9)} Snow et al.¹⁰⁾ obtained varistors in the ZnO–CoO–PbO–Bi₂O₃ system, which were prepared at low temperatures by hot pressing. They found that the non-linear coefficient in the ZnO–CoO–PbO system was higher than that in the ZnO–CoO–Bi₂O₃ system. PbO has similar properties to Bi₂O₃ and Pr₆O₁₁ in phase relation with ZnO, as found in the PbO–ZnO phase diagram.¹¹⁾ This suggests that PbO also may primarily bring about the non-ohmic I – V behavior in ZnO like Bi₂O₃ and Pr₆O₁₁. As far as the authors know, however, sintering behavior and electrical properties of ZnO–PbO have never been investigated. From this viewpoint, microstructure and electrical properties in the ZnO–PbO binary system are investigated in this study. Sintered bodies of ZnO– x mol% PbO ($x=0$ –5) were prepared at various temperatures. Density, grain size and microstructure of the sintered body were examined in detail, and the relationship between those properties and electrical properties were discussed.

2. Experimental

ZnO powder (Wako Pure Chemicals, 99.9%) and β -PbO (yellow) powder (Rare Metallic, 99.9%) were used as starting materials. The ZnO and PbO powders weighed for a specific composition were mixed and pressed isostatically at

200 MPa in the shape of a cylinder. The cylinder was pre-fired at 1073 K for 1 h and then pulverized in a zirconia mortar. The powder was pressed again in the same way. The cylinder was placed in an Al₂O₃ crucible with lids on to reduce the evaporation loss of PbO as less as possible, and was fired for 1 h at a temperature of 1273 to 1573 K, which is higher than the melting temperature of PbO. Since liquid PbO has a relatively high density, gravity segregation occurred in all the sintered bodies of the ZnO–PbO composites. Therefore, every sample for measuring electrical properties was cut off from the center of a sintered body after measuring the density of the sintered body by Archimedeian method. The concentration of PbO is influenced by the evaporation loss in samples for density measurements and by both the evaporation loss and the gravity segregation in samples for electrical property measurements. However, the influences are ignored in this study, because PbO did not occupy large volumes in the ZnO–PbO composites, e.g., 3.1 vol% in the maximum addition 5 mol% PbO and the samples were prepared so that the influences were reduced as stated above.

To characterize sintered bodies, they were surveyed metallographically with an electron probe microanalyzer (JEOL, JXA-733; Tracor Northern, EDS442J). Samples for resistivity measurements were disk about 12 mm in diameter and 0.5 mm thick. Ag films as collecting electrodes were evaporated onto the both surfaces of each disk, and two Au lead wires used for supplying current and detecting voltage drop were attached to the films with Ag paste. Measurements of current-voltage characteristics were made at room temperature with a current/voltage supplier and monitor (Advantest, TR6143), in which voltage was applied at a scanning rate of 1 V·s^{–1}.

3. Results and discussion

3.1. Relative density

Dense sintered body was obtained for pure ZnO in the temperature range examined, but not for ZnO containing PbO. The effect of PbO on the relative density of ZnO–PbO composites fired at 1273 to 1573 K is shown in Fig. 1. The relative density was calculated using the density values 5.642 g·cm^{–3} for ZnO¹²⁾ and 9.56 g·cm^{–3} for β -PbO.¹³⁾ A

decrease of the density by adding PbO is greater than that of Bi_2O_3 .^{14),15)} A small addition of PbO caused poor sinterability to the composites. The vapor pressure of liquid PbO calculated from the thermochemical data¹⁶⁾ is 23 to 1817 Pa at temperatures of 1273 to 1573 K, and that of liquid Bi_2O_3 is 0.04 to 9.7 Pa. Porosity was not reduced at higher temperatures due to such high vapor pressure of liquid PbO. For the ZnO-PbO composites, their relative density, which was independent of the PbO content, increased with an increase of the sintering temperature, and became fixed at about 76% above 1370 K.

3.2. Microstructure

The grain size of composites was influenced by the PbO content and the sintering temperature. The grain size of the ZnO-PbO composites sintered at 1323 K and ZnO-4 mol% PbO sintered at various temperatures are shown in Fig. 2.

Fig. 1. Effect of PbO addition on the relative density of the ZnO-PbO composites sintered at 1323 K.

The grain size increased with an increase of the sintering temperature. The addition of PbO strongly suppressed the grain growth, and the grain size was about 2 μm above 1 mol% of PbO. This tendency is reverse to that in Bi_2O_3 addition.^{14),15)} The microstructure of ZnO-4 mol% PbO is shown in Fig. 3. The micrographs shown in Figs. 3(a) and (b) are fracture surfaces of the composites sintered at 1323 K and 1573 K, respectively. At 1323 K, the composite was not fully sintered and ZnO grains were in the form of rod like parallelepipeds. At 1573 K, ZnO grains greatly grew and fully coalesce each other. As shown in Figs. 3(c) and (d), PbO-rich liquid phases existed between ZnO grains, especially at the intersections of free grains forming triangular prisms. The ratio Zn/Pb in the liquid phases

Fig. 2. Effect of PbO addition (○) and sintering temperature (●) on the average grain size of ZnO-PbO.

Fig. 3. Microstructure of ZnO-4 mol% PbO: (a), (b) secondary electron images of fracture surfaces of samples sintered at 1373 and 1573 K, respectively; (c) back-scattered electron image of a cross section of a sample sintered at 1473 K; (d) distribution image of Pb corresponding to (c).

ranged from 0.25 to 0.43. The dihedral angle between two solid grains and a liquid in equilibrium determines a grain boundary configuration in a composite obtained by the liquid phase sintering. If the dihedral angle is less than 60° , the liquid phase is stable along any length of grain edge forming triangular prisms at the intersections of free grains; if it is between 60° and 120° , the liquid phase partially penetrates along the grain intersections.¹⁷⁾ The averaged value of the dihedral angle was about 60° for ZnO-4 mol%PbO shown in Fig. 3(c). This indicates that many ZnO grains can be surrounded by the liquid PbO-rich phase. This liquid PbO-rich phase penetrated between ZnO grains prevented direct contacts between ZnO grains and resulted in the suppression of grain growth as shown in Fig. 2.

3.3. Electrical properties

Non-linear behavior was observed in I - V curves measured for the all ZnO-PbO composites. I - V curves of ZnO-PbO sintered at 1323 K are shown in Fig. 4 and those of ZnO-4 mol%PbO obtained at various sintering temperatures are shown in Fig. 5. I - V curves had hysteresis. The hysteresis decreased with increasing voltage scan rate. The faster the voltage scan rate is, the lower the electric energy applied to a sample is. Therefore, the hysteresis is probably due to the temperature rise of samples caused by Joule heat. The temperature rise measured at a sample surface was below 3°C at a voltage scan rate of $1\text{ V}\cdot\text{s}^{-1}$ in this study. As shown in Fig. 4, the slope in the I - V curves of ZnO-PbO was much gentler than that of pure ZnO and increased with PbO content. Similar change with the PbO content was also observed at a sintering temperature of 1373 K, but not at 1273, 1473 and 1573 K. The slope in the I - V curves of ZnO-4 mol%PbO increased with an increase of the sintering temperature as shown in Fig. 5. Resistance of ZnO-PbO composites was represented by a series connection ZnO grain/Pb-Zn-O grainboundary layer. Since grain growth at higher sintering temperatures results in a decrease of the number of grainboundary layers in Pb-Zn-O having much higher resistivity than ZnO, the resistance must decrease with an increase of the sintering temperature, and hence the higher the sintering temperature is, the steeper the slope is.

The dependence of the resistivity of the composites on the sintering temperatures is shown in Fig. 6. The resistivity of

the composites is obtained from the slope of the I - V curve within $\pm 100\text{ V}\cdot\text{cm}^{-1}$. The resistivity of pure ZnO is almost fixed for the sintering temperature rise. Its relative density is constant in the sintering temperature range as shown in Fig. 1, and the number of the grainboundary decreases because of the grain growth. Therefore, the grainboundary of pure ZnO has not any effects on its resistivity. The resistivity of the ZnO-PbO composites decreased with an increase of the sintering temperature and approached that of pure ZnO. This is due to a reduction of the number of grainboundary layers by the grain growth as stated above. The resistivities of ZnO-PbO increased with an increase of the PbO content at sintering temperatures of 1323 and 1373 K, but were not dependent on the PbO content at 1273, 1473 and 1573 K. The effect of PbO content on the resistivity is much weaker than that of the porosity in the composites.

The resistivity of the all composites sintered at 1273 to 1573 K is plotted against the relative density in Fig. 7. The

Fig. 5. I - V curves of ZnO-4 mol%PbO sintered at various temperatures.

Fig. 4. I - V curves of ZnO-PbO sintered at 1323 K. The insert schematically shows an I - V curve and the sequence of the voltage scan.

Fig. 6. Effect of sintering temperature on the resistivity, ρ , of ZnO-PbO.

Fig. 7. Relation between relative density and resistivity, ρ , for ZnO-PbO sintered at various temperatures. The numbers in the figure correspond to the PbO concentrations.

resistivity rose moderately to about 75% with a decrease of the relative density, and it increased abruptly near 70%. Such a drastic resistivity change is caused by the disconnection of electrical passes between ZnO grains and/or between Pb-Zn-O phase and ZnO grain in high porosity. According to percolation theory on the resistivity of composites,^{18),19)} the resistivity of a composite consisting of non-conductive phases and randomly oriented conductive phases is represented by the equation

$$\rho_m = \rho_1 \left(1 - \frac{f}{f_c}\right)^{-f_c/(1-L)} = \rho_1 \left(1 - \frac{f}{f_c}\right)^{-t} \quad (1)$$

where ρ_m is the resistivity of the composite, ρ_1 the resistivity of the conductive phase, f the volume fraction of the non-conductive phase, f_c the critical (percolation) volume fraction for the non-conductive phase, L the effective demagnetization (depolarization) coefficient characterizing the conductive phase, t the exponent ($=f_c/(1-L)$). In the ZnO-PbO composites, PbO-rich grainboundary phases and pores are corresponding to the non-conductive phase and ZnO grains the conductive phase. Since the volume of the PbO-rich phases is very small as shown in Fig. 3(c), the porosity is regarded as the volume fraction of the non-conductive phase. The solid curve in the figure was obtained by fitting Eq. (1) for the data under $f_c = 0.29$ corresponding to a relative density of 71%. The best fitting gave the parameters $\rho_1 = 1 \times 10^4 \Omega \cdot \text{cm}^{-1}$, $t = 1.84$ and $L = 0.84$. The L value is theoretically 1/3 and 1/2 for conductive phases in the shapes of spheres and disks, respectively. Higher values than 1/2 mean that conductive phases are ellipsoid,¹⁹⁾ which is consistent with the shapes of ZnO grains shown in Fig. 3(a).

The current-voltage characteristic of a varistor at a breakdown region is generally approximated by the equation,

$$I = I_c \left(\frac{V}{V_c}\right)^\alpha \quad (2)$$

where I_c is a critical current as a standard value, V_c a critical voltage at I_c and α a nonlinear constant. In this study, the critical current could not be determined, because the range of the applied current is very different in each sample.

Fig. 8. Effects of PbO addition (a) and sintering temperature (b) on the non-linear coefficient of ZnO-PbO sintered at various temperatures. The solid curve and the break line correspond to the ZnO-PbO composites and pure PbO, respectively.

Therefore, a nonlinear constant α in an I - V curve in a breakdown region was determined from the maximum slope in the $\log I$ - $\log V$ curve. The dependence of α on the PbO content and the sintering temperature are shown in Figs. 8(a) and (b), respectively. Pure ZnO showed weak non-linearity in its I - V curve and had α values less than 2. A single ZnO-phase grain itself in a ZnO-Bi₂O₃-CoO-MnO-Sb₂O₃ varistor with a high α value has an ohmic property.⁸⁾ These indicate that for pure ZnO the grainboundaries give weak non-linearity to its I - V curve. The non-linear coefficient of ZnO-PbO, which was a little higher than that of pure ZnO, ranged almost from 2 to 3 and hardly depended on the PbO content and the sintering temperature. The non-linear coefficient of ZnO-PbO-CoO ceramics¹⁰⁾ is considerably bigger than that of ZnO-PbO obtained in this study. CoO hardly influences the non-linearity of ZnO.⁹⁾ Adding CoO to ZnO-Bi₂O₃ significantly raised the non-linear coefficient.^{3),8),9)} Bi₂O₃ has a weak effect on the non-linearity in the ZnO-Bi₂O₃ system.^{3),9)} In the I - V behavior of ZnO ceramics, therefore, the role of PbO is very similar to that of Bi₂O₃.

4. Conclusions

In this study, ZnO doped with PbO in the range of 0.5 to 5 mol% were prepared by sintering at temperatures of 1273 to 1573 K, and their microstructure and electrical properties were examined. Pure ZnO was fully sintered in the temperature range. By adding PbO to ZnO, the relative density was greatly decrease due to the high vapor pressure of liquid PbO. In the ZnO-PbO composites, liquid Pb-Zn-O phase penetrated between ZnO grains and prevented the grain growth of ZnO. The ZnO-PbO composites revealed non-linear behavior in I - V characteristics. The resistivity of the ZnO-PbO composites decreased and approached that of

pure ZnO with an increase sintering temperature. The non-linear coefficient of the ZnO–PbO composites ranges from 2 to 3, and hardly depends on the PbO content and the sintering temperature.

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