Microstructural and electrical characteristics of SiO₂ doped ZnO–Bi₂O₃ varistors

R GOEL, A SIL* and H R ANAND

School of Basic and Applied Sciences, Thapar Institute of Engineering and Technology, Patiala 147 001, India

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Abstract. Varistors in the new system ZnO–Bi₂O₃–SiO₂ were prepared through conventional ceramic processing route. The effect of sintering temperature and time (0.5 h to 2 h between 1000° and 1250°C) on the microstructure and current/voltage characteristics of the varistors of the new system were investigated and the results were compared with those of ZnO–Bi₂O₃ system varistors prepared. An increase in nonlinear coefficient (α) value was observed in the SiO₂ added varistors. The microstructure and the phase of the varistors were examined by means of SEM and XRD. The Zn₇SiO₄ spinel phase was found to be present in the intergranular region. The grain growth exponent was determined to be 2.5 ± 0.2 and the activation energy for the ZnO grain growth was estimated to be 251 ± 11 kJ/mol. These values were compared with those estimated for ZnO–Bi₂O₃ system varistors.

Keywords. Varistors; nonlinear coefficient; sintering; grain sizes.

1. Introduction

Zinc oxide based varistors are basically polycrystalline semiconducting devices having highly nonlinear current–voltage characteristics (Levinson and Philip 1977; Castro *et al* 1992). These devices are used predominantly for circuit overvoltage protection with applications ranging from a few volts in electronic circuits to millions of volts in high tension distribution lines. Varistors are directly connected across the power line in parallel with the load to be protected (Levinson and Philip 1986). The varistor normally operates in the prebreakdown region. By virtue of their ceramic nature, varistors can be fabricated into a variety of sizes and shapes, and this feature facilitates a high degree of user flexibility (Castro *et al* 1992). Most commonly used varistors are produced by sintering ZnO powder together with small amounts of other oxide additives such as Bi₂O₃, MnO₂, CoO, Sb₂O₃, NiO, BaO and Cr₂O₃ (Levinson and Philip 1986; Gupta 1990). These oxide additions can affect the varistor properties in two ways: (i) directly, in an electrical sense, as in the case of Bi₂O₃, which segregates at the ZnO grain boundaries and relates to the nonlinearity of the current voltage characteristics, or (ii) indirectly, by affecting the microstructural development of ceramic body during firing. One interesting group of additive oxides is that which reacts with ZnO to form a second phase with the spinel structure, including Sb₂O₃ (Zn₇Sb₂O₁₂), Al₂O₃ (ZnAl₂O₄), TiO₂ (Zn₂TiO₄), and Nb₂O₅(Zn₃Nb₂O₈). The role of Bi₂O₃ in the grain growth

process of ZnO was already reported by many researchers (Matsuoka *et al* 1969; Mukae *et al* 1977; Matsuoka 1981; Cerva and Russwurm 1988). Segregation of some of the dopants at the grain boundaries of ZnO is believed to be essential for nonohmic properties of varistor. In the present study, ZnO–Bi₂O₃ varistors were fabricated with silica (SiO₂) additive (Kim *et al* 1989; Chiou *et al* 1990; Senda and Bradt 1990; Dey and Bradt 1992; Nunes and Bradt 1995) with a view to possibly substitute the usually reported spinel forming compound and to investigate the effect of SiO₂ on the grain growth process and hence on the electrical characteristics of the ZnO based varistors. The system of typical composition of 99 mol% ZnO–0.5 mol% Bi₂O₃–0.5 mol% SiO₂ has been chosen to address the objectives of the present work.

2. Experimental

2.1 Specimen preparation

Reagent grade raw materials, in the proportion of 99 mol% ZnO, 0.5 mol% Bi₂O₃ and 0.5 mol% SiO₂ were weighed and mixed by wet milling (using centrifugal ball mill) with zirconia media (balls and vessels) for 30 min. Powders were then air dried. Particle size distribution of the ZnO powder was 1 µm and less. Pellets (16 mm in diameter and about 2 mm thick) were prepared by using a hydraulic press with an applied load of 150 kN yielding green densities of about 60% of theoretical density. Density measurement was based on Archimedes principle. Samples were sintered in the temperature range between 1000°C and 1250°C for time period

*Author for correspondence

ranging between 0.5 h and 2 h in air with a heating and cooling rate of about 10°C/min.

2.2 Microstructural observations

The microstructure was examined by scanning electron microscope (SEM) (Model JEOL 840A). Grain sizes were measured directly from the photomicrographs of the samples. Linear interception method was used for these measurements. The average grain size ($\bar{G}$) was calculated by employing the following formula as described by Mendelson (1969):

$$\bar{G} = 1.56 \bar{L},$$

where $\bar{L}$ is the average grain-boundary intercept length of a series of random lines drawn on the micrograph.

2.3 V-I characteristics measurement

The pellets were coated on both sides with conductive silver for good ohmic contact formation. The V-I characteristics of the samples were measured using a dc power supply. The most important parameter of varistor is nonlinear coefficient, α which is defined by empirical relation,

$$I = KV^\alpha,$$

where I is the current, V the applied voltage, and K a constant. The α value is estimated between two desired magnitudes of current and corresponding voltages by employing the relation

$$\alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)},$$

where I_1 and I_2 are the currents at voltages V_1 and V_2 ($V_2 > V_1$) (Gupta 1990).

3. Results and discussion

3.1 Grain growth of ZnO

Microstructures of the specimens of ZnO-Bi₂O₃ (0.5 mol%)-SiO₂ (0.5 mol%) and ZnO-Bi₂O₃ (0.5 mol%) systems sintered at 1250°C for different time intervals of 0.5, 1, 1.5, 2 h are shown in figures 1 and 2, respectively. Table 1 presents the grain size values for samples of ZnO-Bi₂O₃-SiO₂ system sintered at temperature 1250°C for time periods ranging between 0.5 h and 2 h. As expected the average grain size increases with increasing soaking time. It is evident from figure 1 that the intergranular regions are predominantly occupied by

the spinel phase Zn₂SiO₄. It is shown later that the above phase along with pure ZnO phase were detected by means of XRD in the specimens. The presence of silica-rich phase at the grain boundaries is also evidenced from the EDS spectrum taken at the grain boundaries (figure 5a) and the same was compared with the spectrum taken in the grain (figure 5b). In figure 2, grain boundaries are found to be very distinct as observed for ZnO-Bi₂O₃ system by other researchers (Gupta and Coble 1968; Readey *et al* 1988; Senda and Bradt 1990).

3.2 Pore characteristics

Presence of pores in all the samples of ZnO-Bi₂O₃ system and even pure ZnO was observed in almost all the studies by previous researchers. Senda and Bradt (1990) attributed this to the possibility of a higher level of volatility of Bi₂O₃ at higher temperatures. Gupta and Coble (1968) and Readey *et al* (1988) observed increases in pore sizes at high temperatures in pure ZnO and concluded that it may have been caused by impurity evaporation or perhaps even evaporation of the ZnO itself. Although pores were also observed in the present study as can be seen in figure 2 for the ZnO-Bi₂O₃ samples, the level of porosity seems to be much less as compared to that reported by others (Senda and Bradt 1990). The samples prepared with SiO₂ as an additive (0.5 mol% in the present study) were found to be almost free of pores (within the grains as well as at the grain boundaries) as is evident from the micrographs given in figure 1.

3.3 Activation analysis of kinetic grain growth parameters

3.3a Determination of grain growth index (n): The grain growth (isothermal) process can be analysed by using the general phenomenological kinetic grain growth equation:

$$G^n - G_0^n = k_0 t \exp(-Q/RT), \quad (1)$$

where G is the average grain size at time t , G_0 the initial grain size (at $t=0$), n the kinetic grain growth exponent, k_0 a pre exponential constant, Q the apparent activation energy for grain growth, R the gas constant, and T the absolute temperature. When G_0 is small compared to G , at some time t , the factor G_0^n can be neglected relative to G^n and (1) simplifies to

$$G^n = k_0 t \exp(-Q/RT). \quad (2)$$

Taking natural log on both sides of (2) we get,

$$n \ln G = (\ln k_0 - Q/RT) + \ln t. \quad (3)$$

Figure 1. a-b.

Figure 1. Scanning electron micrographs from varistor specimens of ZnO -0.5 mol% Bi_2O_3 -0.5 mol% SiO_2 system sintered at 1250°C for time period (a) 0.5 h, (b) 1.0 h, (c) 1.5 h and (d) 2.0 h.

Figure 2. a-b.

Figure 2. Scanning electron micrographs from varistor specimens of ZnO-0.5 mol% Bi₂O₃ system sintered at 1250°C for time period (a) 0.5 h, (b) 1.0 h, (c) 1.5 h and (d) 2.0 h.

In figure 3a, $\ln G$ vs $\ln t$ is plotted for the specimens (ZnO-Bi₂O₃-SiO₂) sintered at 1250°C. Although one can obtain the plots for the samples sintered at other temperatures, the grain growth behaviour at 1250°C is chosen here because at this temperature silica is found well in its softening state (in the vicinity of the melting point). The value of n obtained from the plot is 2.5 ± 0.2 , whereas the corresponding value of n obtained for the ZnO-Bi₂O₃ system was found to be 3.3 ± 0.2 .

Table 1. Grain sizes developed during sintering at 1250°C for different soaking times.

Soaking time (h)	Grain size (μm)
0.5	26.7
1.0	27.9
1.5	32.9
2.0	46.4

Figure 3. a. $\ln G$ vs $\ln t$ plot for the ZnO-0.5 mol% Bi₂O₃-0.5 mol% SiO₂ varistor samples sintered at 1250°C and b. $\ln (G^{2.5}/t)$ vs $1/T$ Arrhenius plot for ZnO grain growth (soaking time = 2 h).

3.3b Determination of Q : Equation (2) can be expressed as

$$\ln (G^n/t) = \ln k_0 - Q/R(1/T).$$

Figure 3b shows the plot of $\ln (G^{2.5}/t)$ vs $1/T$ for samples sintered at temperatures ranging between 1000°–1250°C for soaking time of 2 h. The value of Q from the plot is obtained as 251 ± 11 kJ/mol. The value of Q for ZnO-Bi₂O₃ system has been found to be 122 ± 41 kJ/mol. Thus even with a minute amount of silica addition the activation energy requirement becomes doubled. This is perhaps due to the fact that the silica at relatively high temperature (specifically above the glass transition temperature of silica) acts as viscous medium and the diffusivity of Zn²⁺ ions becomes restricted through the intergranular layer.

3.4 Phase identification and effect of silica

The X-ray powder diffraction pattern of samples was recorded on a X-ray diffractometer (Model: Rigaku D-Max IIIC) and a representative pattern for ZnO-Bi₂O₃-SiO₂ specimen sintered at 1250°C for 2 h is shown in figure 4. The peaks of ZnO are found to appear predominantly. In addition there are appearances of peaks of Zn₂SiO₄ phase which has a spinel structure. However, the intensity of these peaks is understandably low because of low concentration of silica (0.5 mol%). On examination of SEM micrographs (figure 1), it can be observed that the silica-rich phase is present largely in the intergranular region of the samples. This has further been confirmed by EDS study (figures 5a and b) which shows the presence of more pronounced Si peaks at the grain boundary as compared to Si peaks within the grain.

3.5 V - I characteristics

The current vs voltage variation was plotted in the form of $\ln V$ vs $\ln I$. In order to check the optimum performance of varistors, the V - I characteristics were studied for the specimens sintered at various combinations of time and temperature parameters. Typical plots are shown in figure 6 for the samples sintered at 1250°C for two different soaking time periods of 0.5 h and 2 h. The nonlinear coefficient (α) values estimated from the V - I characteristics were found to lie in the range 4–15 for the varistors in the system ZnO-Bi₂O₃-SiO₂ whereas in case of ZnO-Bi₂O₃ samples made, the values of α lie between 4 and 8. These α values were estimated from the relatively flat middle portions of the V - I curves i.e. from the region starting in each case with $\log I = 0.8$. Table 2 presents the values of α for the two systems showing an average increase in the performance of the varistors in the SiO₂ added ZnO-Bi₂O₃ system. It can be seen from figure 6 that though the small addition (0.5 mol% in the present study) of SiO₂ improves (increase) the α values only modestly, however, the

Figure 4. X-ray diffraction pattern of the varistor specimen in the system ZnO-0.5 mol% Bi₂O₃-0.5 mol% SiO₂ sintered at 1250°C for 2 h.

Figure 5. EDS, (a) taken at the grain boundaries and (b) taken within the grain of ZnO-0.5 mol% Bi₂O₃-0.5 mol% SiO₂ system varistor specimen sintered at 1250°C for 2 h.

Table 2. Values of non-linear coefficient of $V-I$ characteristics of the specimens sintered at 1250°C.

Soaking time (h)	α values for	
	ZnO-Bi ₂ O ₃ varistors	ZnO-Bi ₂ O ₃ -SiO ₂ varistors
0.5	8.1	8.5
1.0	4.7	11.3
1.5	3.8	3.4
2.0	6.2	15.2

Figure 6. Log-log plots of current versus applied voltage of varistor specimens sintered at 1250°C for 0.5 and 2.0 h.

range of nonlinear operation (flatness of the curves) of the varistors with SiO₂ added system increases significantly (as compared to the SiO₂ free system), extending over three orders of current magnitude. For the base ZnO-Bi₂O₃ system varistors, the $V-I$ characteristics show their flatness over a smaller range of current magnitude (only one order).

It may be mentioned again that only the composition of SiO₂ added system (i.e. 99 mol% ZnO-0.5 mol% Bi₂O₃-0.5 mol% SiO₂) was investigated and presented in this paper. However, one can always vary the percentage of SiO₂ content within the limit of solid solubility of SiO₂ in the host material ZnO so as to optimize the presently proposed varistor system composition for which α value reaches its maximum.

4. Conclusions

(I) The average grain size increases with increasing sintering time. The grain size exponent (n) for the

samples sintered at 1250°C is found to be 2.5 ± 0.2 . The activation energy (Q) for grain growth is estimated as 251 ± 11 kJ/mol for the samples sintered for 2 h.

(II) The samples prepared with SiO₂ are found to be almost free of pores. The XRD studies reveal the formation of Zn₂SiO₄ compound at the grain boundaries on heating the samples above 1200°C.

(III) The nonlinear coefficient (α) values for the silica doped samples when sintered at 1250°C for the time period between 0.5 and 2 h, lie between 4 and 15 whereas the α values for silica free samples lie in the range 4–8.

(IV) Intergranular silica rich phase inhibits not only the mass transport of Zn ions but also electron transport by offering high electrical resistance. Therefore the overall effect makes the varistors (with silica additive) to have better performance as characterized by higher α values.

(V) Thus the overall performance of varistors improves on addition of even very small quantity of SiO₂.

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