Microstructure and Current-Voltage Characteristics of Erbium Oxide Doped Multicomponent Zinc Oxide Varistors

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Abstract: The present work emphasizes the influence of Er_2O_3 addition on the microstructure and nonlinear current-voltage characteristics of ZnO based varistors prepared by mixing in a high energy ball mill followed by compaction and sintering at a temperature of 1100 °C for duration ranging from 0.5 to 8 h. Increasing sintering time is found to enhance the size of ZnO grains of the sintered pellets and thereby, degrades the electrical properties. However, Er_2O_3 addition retards the grain growth of ZnO due to the generation of secondary spinel phases ($ErVO_4$ and Er-rich) at grain boundaries and triple points that restrict the grain boundary migration. Er_2O_3 modified ZnO varistor sintered at 1100 °C for 0.5 h exhibits considerably improved electrical property with nonlinear exponent and breakdown field of 27 and 3880 V cm^{-1}, respectively.

1. Introduction

Varistors or variable resistors are voltage dependent switching devices in which their resistance varies (from 10^{12} to 1 Ωcm) instantaneously (almost in picoseconds) in response to the change in voltages appearing across it [1, 2]. Above a certain threshold voltage, known as the breakdown voltage (V_b), their resistance reduces substantially which allows the current to flow through the varistor rather than the main electrical circuit. As a result, varistors are extensively used as an important element of lightning arrester in electrical power systems and as surge absorber in electronic circuits due to their excellent nonlinear properties, quick response in transient voltage and high surge energy absorption capability ranging from a few joules to thousands of joules [3]. Microstructurally varistors consist of semiconducting *n*-type ZnO grains with highly resistive grain boundaries [2]. The nonlinear properties are mainly attributed to the double Schottky electrical potential barrier at the grain boundaries due to the segregation of large ionic forming oxides [4,5]. Multicomponent varistors are generally prepared by sintering of ZnO powder combined with a number of other minor additives such as Bi_2O_3, Sb_2O_3, V_2O_5, Pr_6O_{11} *etc* [6]. Microstructure of ZnO-based varistor is important since it controls electrical properties. Specifically, the average grain size of the varistor ceramics is crucial, because it is well established that the breakdown voltage of a varistor is inversely related with its grain size. In other words, the grain growth should be minimized during consolidation process to achieve a better varistor property. It is reported that rare earth (Er, Y, Dy, La and Tb) oxides are grain growth inhibitor [7,8]. These oxides restict the mobility of grain boundaries and hence, limit the grain coarsening during sintering. In recent times, continued efforts have been directed to develop high performance varistors specifically by improving the nonlinear property with proper dopant addition. Nahm [9] has proposed that of rare earth oxides doping not only restricts the grain boundary migration but also improves nonlinear propertiesand stability against DC accelerated ageing stress. Beneficial effects of Erbium oxide (Er_2O_3) on microstructural characteristics and nonlinear electrical property of Zinc oxide based varistors have been highlighted in some recent investigations [10,11]. However, little efforts have been directed till date to understand the influence of isothermal sintering duration on structure and property of Er_2O_3 modified ZnO-based varistor ceramics.

Considering the present state of understanding, this work aims to investigate the role of sintering duration of ball milled varistor powder mixtures. The emphasis has been directed to understand the influence of Er_2O_3 addition on microstructural characteristicsand nonlinear current-voltage properties of multicomponent ZnO-based varistors with reference to Er_2O_3 free samples.

2. Materials and Methods

In the present study, varistors have been developed by using the high purity (≥ 99.9%) oxide powder mixtures available commercially with a nominal composition of (97.4 – *x*) mol.% ZnO, 0.5 mol.% V_2O_5, 2.0 mol.% MnO_2, 0.1 mol.% Nb_2O_5 and *x* mol.% Er_2O_3 (x = 0.0 and 0.5). The process of preparing the varistor is comprised of mixing all the powders for a predetermined time of 35 h in a high energy ball milling with a ball to powder ratio of 16:1. The ground powders have been compacted into disc shaped pellets with a diameter of 10 mm and thickness around 3 to 4 mm on a hydraulic press at a pressure of 500 MPa. All the pellets have been subjected to sintering at a temperature of 1100 ^{o}C for various times (0.5 to 8 h). The uniformity of heating and cooling the specimen has been maintained throughout the sintering process at a rate of 5 ^{o}C min^{-1}. The sintered pellets have been measured for their bulk density based on Archimedes principle in the microbalance using deionized water as liquid medium. The formation of different phases in the varistor pellets has been determined by using X-ray diffraction (XRD) technique. The surface microstructures of the sintered pellets have been examined by a field emission scanning electron microscope (FESEM). Reduction of adverse effects due to charging and improving the resolution of the recorded microstructure has been done by coating of thin Pt alloy layer on the sintered pellets. Spectrometric analysis has been performed at a particular area of interest for selected samples using energy dispersive spectrometer (EDS) attached with the FESEM unit. Linear intercept method has been used to measure the average grain size *(d)* of the recorded microstructures. A minimum of ten randomly taken FESEM images have been used to find the average grain size based on the following relation [7]:

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

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 the line length *L*. The nonlinear electric field-current density (*E*-*J*) characteristics were measured using a high voltage source-measurement unit. The breakdown field (E_{1mA}) has been determined at a current density of 1.0 mA cm^{-2} and the nonlinear exponent (α) has been estimated from the following expression [12]:

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

where, E_1 is the electric field at J_1= 1.0 and E_2 are the electric fields at J_2= 10 mA cm^{-2}.

3. Results and Discussion

A set of FESEM microstructures in Fig. 1 illustrates the effect of sintering time and Er_2O_3 addition on densification and mean grain size of the sintered ZnO pellets. All the sintered pellets reveal a well-defined grain structure (Fig. 1). Microstructure of the sintered pellets consists of uniformly distributed homogeneous ZnO grains as a primary phase. The secondary intergranular phases are found to present at the grain boundaries, triple points and occasionally within the grains. With Er_2O_3 addition, the amount of secondary phases increases. The bulk density of all the specimens varies within a narrow range of 97-99% theoretical density; this indicates no significant effect of sintering time on the consolidation process. In contrast, the grain size is found to increase monotonically with increasing sintering time due to obvious grain coarsening. However, Er_2O_3 addition is found to be considerably reduced the grain size at any particular time duration. For example, the mean grain values of Er_2O_3

free and 0.5 mol.% Er_2O_3 added samples are 32.6 and 10.8 µm, respectively, when both pellets were sintered for 8 h. EDS microanalyses results (Fig. 2) corresponding to the intergranular regions of the pellets sintered for 4 h confirm the presence of V, Mn, Nb and O along with Zn in Er_2O_3 free sample as compared to relatively high concentration of Er (33.66 wt.%) in addition to V, Mn, Nb, O and Zn in the Er_2O_3 added ones. These observations indicate that Er_2O_3 mainly presents at the grain boundaries and triple points.

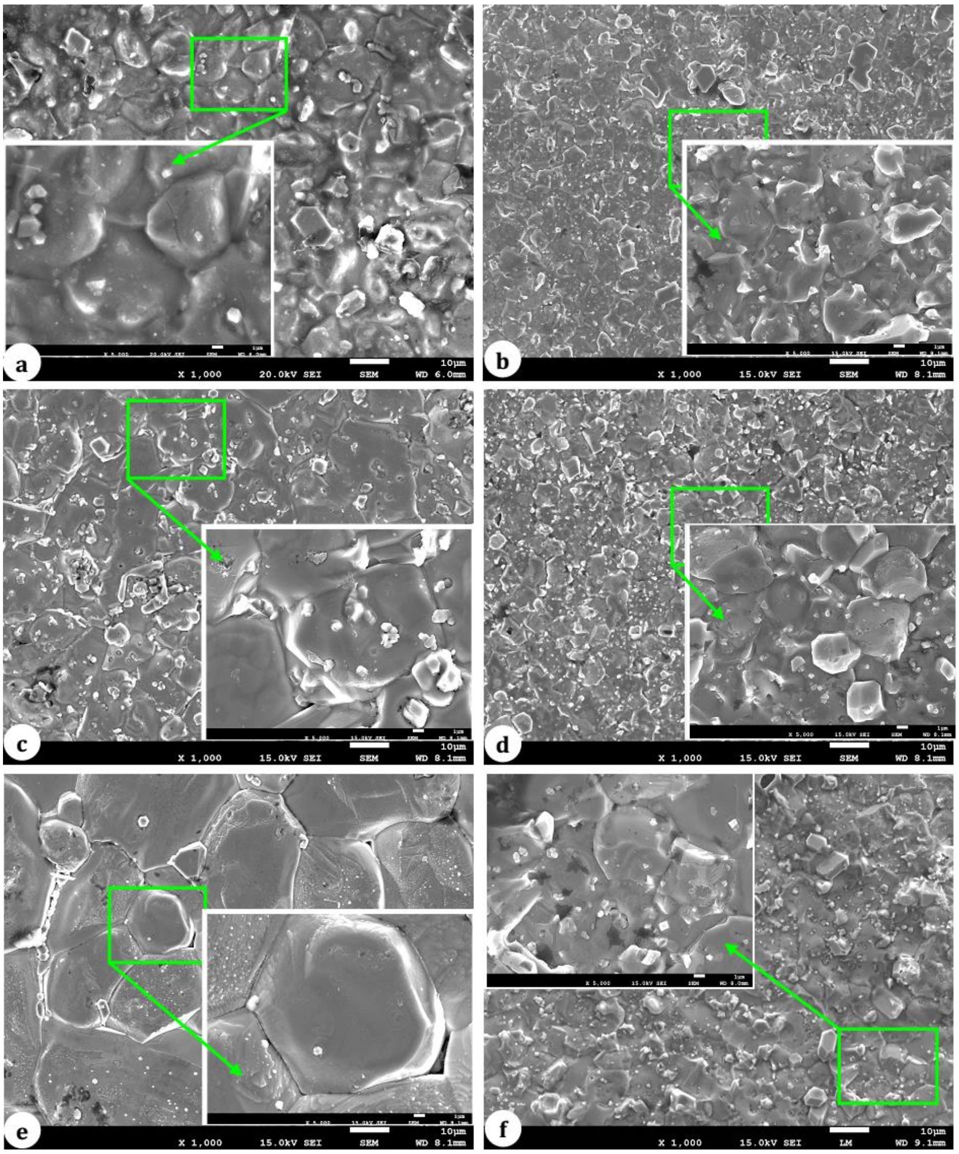

Figure 1. FESEM micrographs of Er_2O_3 free varistor pellets sintered for (a) 0.5 h, (c) 2 h and (e) 8 h, and 0.5 mol.% Er_2O_3 added pellets sintered for (b) 0.5 h, (d) 2 h and (f) 8 h. Inset images at 5 kX exemplify the effects of sintering time and Er_2O_3 addition on grain size.

All the developed phases in the varistor pellets are characterized by XRD analysis. Fig. 3 represents the typical XRD patterns of some selected sintered pellets. The secondary phases like $Zn_3(VO_4)_2$, $Zn_4V_2O_9$,V_2O_5, Zn_2MnO_4 and Mn-rich in addition to primary phase of major hexagonal ZnO has been identified in the Er_2O_3 free sample. The Er_2O_3 added samples additionally reveal the presence of Er related secondary phases like $ErVO_4$ and Er-rich phasesas secondary phases. The Er-rich spinel phases are found to be mainly segregated in the intergranular region of grain boundary area and triple points (Fig. 2). It is worthy to mention here that the intensities of the secondary phases appear to be higher with increasing sintering time and/or Er_2O_3 addition indicating higher degree of formation of secondary phases.

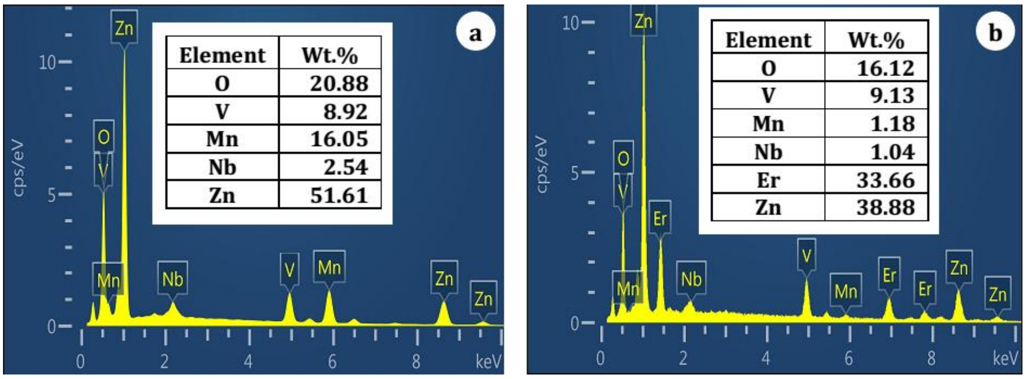

Figure 2. EDS results related to the intergranular layer in the (a) Er_2O_3 free and (b) 0.5 mol.% Er_2O_3 added varistor samples.

Fig. 4 depicts the variations of mean grain size as calculated by image analysis of FESEM micrographs as function of sintering time. It can be observed that with increasing the time of sintering from 0.5 to 8 h, the mean size of ZnO grain increases; however, the rate of grain coarsening is significantly higher for the Er_2O_3 free samples than that of the Er_2O_3 added samples. For the Er_2O_3 free sample, the grain size increases from 10.7 to 32.6 µm, whereas, the grain size increases from 6.3 to 10.8 µm for Er_2O_3 added samples within the investigated sintering time duration. The obtained results assist to conclude that Er_2O_3 segregates at the intergranular layers and forms Er-rich secondary spinel phases. These spinel phases restrict the grain boundary movement [2], and thereby diminishes the degree of grain coarsening during sintering. Therefore, the ZnO grain size is found to be considerably finer for Er_2O_3 added specimens as compared to that of Er_2O_3 free samples at a given sintering duration (Fig. 4). Fig. 5 depicts the grain size distribution of Er_2O_3 free and 0.5 mol.% Er_2O_3 added varistor pellets sintered at a temperature of 1100 °C for 4 h. It can be seen that Er_2O_3 addition results a narrower distribution as compared to Er_2O_3 free sample which indicates the restriction of grain growth during sintering. For example, the grain size distribution range of Er_2O_3 free sample varies from

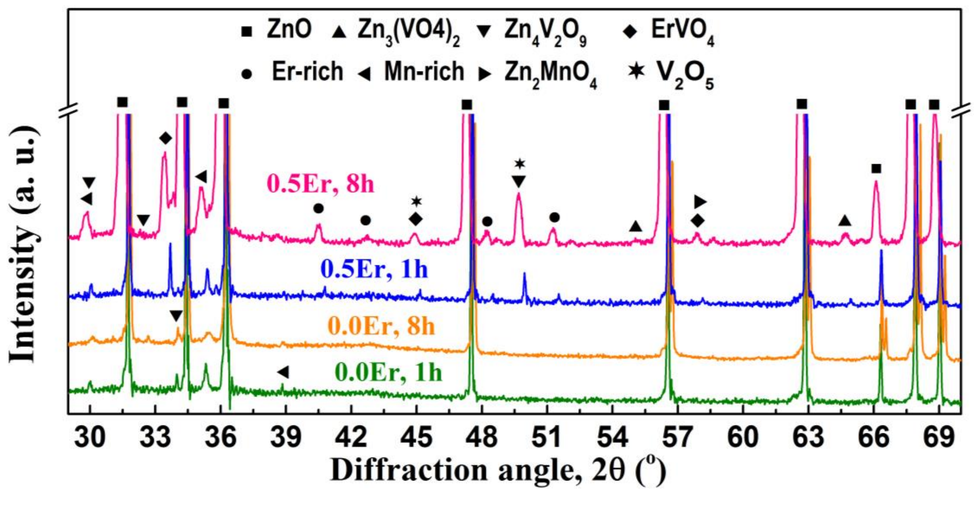

Figure 3.XRD patterns of sintered pellets.

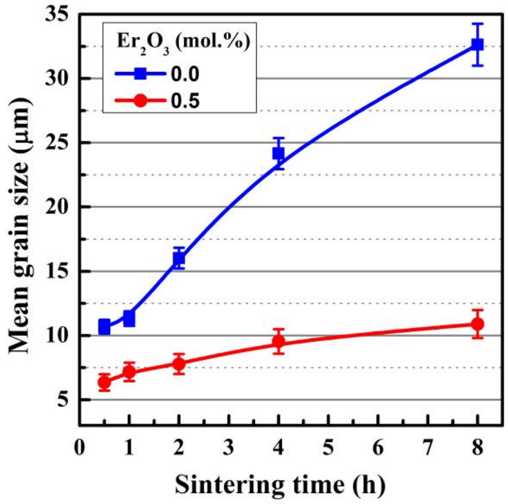

Figure 4. Effect of sintering time with mean grain size of varistor specimens.

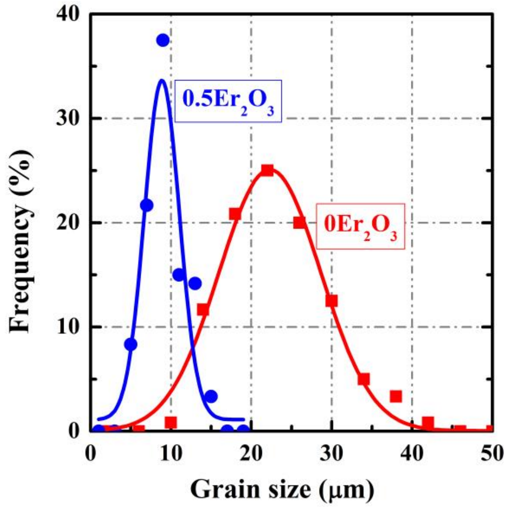

Figure 5. Grain size distribution of the varistor pellets sintered for 4 h.

1.8 to 49.5 µm; whereas, it is limited in between 0.84 to 19 µm for Er_2O_3 added sample. Nahm [12] has reported that incorporation of Er_2O_3 reduces the average grain size of Er_2O_3 doped ZnO varistors.

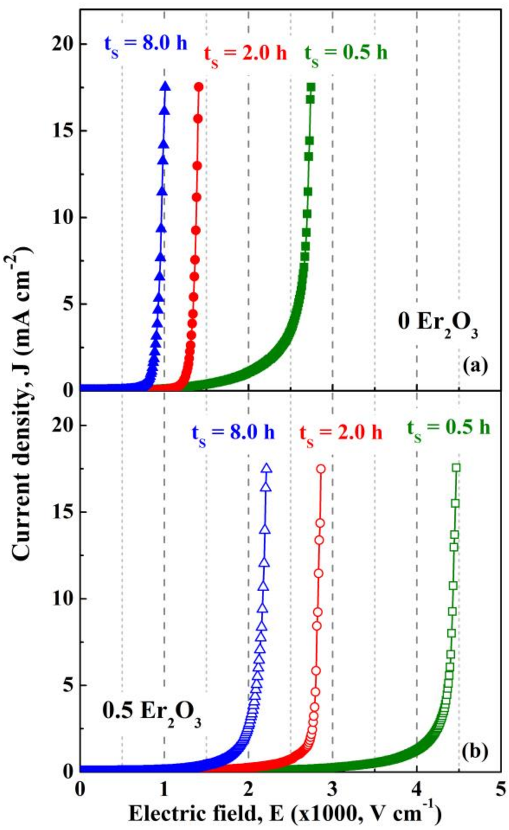

Figure 6. E-J characteristics of (a) Er_2O_3 free and (b) 0.5 mol.% Er_2O_3 added varistor specimens sintered for different time duration.

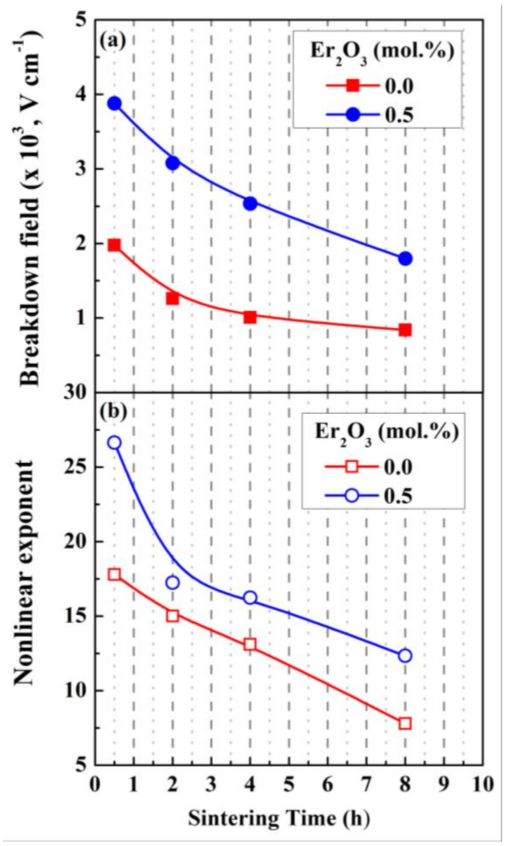

Figure 7. Variations of (a) breakdown field and (b) nonlinear exponent with sintering time.

The nonlinear electrical property of some selected samples is estimated by their electric field–current density (*E–J*) response and the obtained results are shown in Fig. 6. The *E–J* curves are noticeably divided into non-conduction and conduction regions [12].The transition point between these two regions is known as breakdown field (E_{1mA}) [1]. The results in Fig. 6 reveal that the nonlinear property of the selected varistor ceramics enhances due to incorporation of Er_2O_3, however, the same reduces with increasing sintering duration. The magnitudes of the breakdown field (E_{1mA}) andnonlinear exponent (α) are estimated from the *E-J* curves. Fig. 7 graphically represents the variations of the nonlinear parameters (E_{1mA} and α) with isothermal sintering time. Both the obtained breakdown field and nonlinear exponent values are found to reduce continuously with increasing sintering time. The Er_2O_3 addition is found to enhance the electrical property of the varistor pellets. The value of breakdown field and nonlinear exponent increases from 1976 to 3880 V cm^{-1} and 17 to 27 with Er_2O_3 addition for the samples sintered for 0.5 h. Considerable improvement in breakdown field is associated to the reduction of average grain size occurred due to the incorporation of Er_2O_3 (Fig. 4). These observations can be easily explained considering well established relationship [7]:

$$E_{1mA} = V_{gb}/d \qquad (3)$$

where, V_{gb} is the voltage per grain boundary and d is the average grain size. The breakdown field is expected to decrease with increasing average grain size. Therefore, the variation of the nonlinear properties with sintering time (Fig. 6) is quite natural if one considers the effect of sintering time on the size of ZnO grain (Fig. 4). In the present investigation, the Er_2O_3 added varistor sample sintered for 0.5 h exhibits the best nonlinear property witha breakdown field of 3880 V cm^{-1}andnonlinear exponentof 27.

4. Conclusions

The effects of Er_2O_3 addition and isothermal sintering duration (0.5-8 h) on microstructure and current-voltage behaviour of ball milled (35 h) ZnO–V_2O_5–MnO_2–Nb_2O_5 semiconducting varistor powder mixtures have been investigated at sintering temperature of 1100 ^oC.The microstructure of the sintered pellet characterized by FESEM examinations as well as EDS and XRD analyses assist to conclude that varistor samples consists primarily of ZnO grains with secondary spinel phases along the intergranular layers. With increasing sintering time, nonlinearelectrical properties of the investigated varistor ceramics diminish due to coarsening of ZnO grains. Whereas, Er_2O_3 addition enhances the nonlinear electrical properties by reducing the ZnO grain size due to the development of mainly $ErVO_4$ and Er-rich secondary spinel phases which acts like a grain growth inhibitor. ZnO-based varistor sintered at 1100 ^oC for 0.5 hwith 0.5 mol.% Er_2O_3 addition exhibits the best nonlinear electrical properties withhighest electrical field and nonlinear exponent valueof 3880 V cm^{-1} and 27, respectively.

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