



Mechanical Activation of Spinel and Pyrochlore Phases in ZnO Based Varistors

C. GÓMEZ-YÁÑEZ, J. VELÁZQUEZ-MORALES & E.G. PALACIOS

Department of Metallurgical Engineering, ESIQIE-IPN, A.P. 118-593, Zacatenco, Mexico City, 07738, Mexico

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Abstract. Mixtures of ZnO, Sb₂O₃ and Bi₂O₃ powders corresponding to the stoichiometric compositions of Zn₇Sb₂O₁₂ (spinel) and Zn₂Bi₃Sb₃O₁₄ (pyrochlore) were milled in a shaker mill (SPEX) up to 180 minutes. The influence of the mechanical activation of the powders, as a result of the milling, was determined by Differential Thermal Analysis, Thermogravimetric Analysis and X-ray Diffraction. Additionally, in order to compare to commercial recipes the mixture ZnO + 2.7 wt% Sb₂O₃ + 4.5 wt% Bi₂O₃ was milled in a shaker mill up to 180 minutes. Varistor devices were fabricated with both milled and unmilled mixtures. The devices were characterized by I-V studies, Scanning Electron Microscopy and X-ray Diffraction. Mechanical activation on the system ZnO-Bi₂O₃-Sb₂O₃ produced a chemical reaction and amorphization in the powder mixture. The weight loss due to volatilization of Bi₂O₃ and Sb₂O₃ that occurs in both ZnO-Sb₂O₃ and ZnO-Sb₂O₃-Bi₂O₃ systems at temperatures below 1200°C is reduced by milling the powder mixtures.

Keywords: mechanical activation, varistors, ZnO, electroceramics

1. Introduction

A varistor is a polycrystalline ceramic device designed for overvoltage protection. The proper performance of a varistor resides on the characteristics of the grain boundary where a potential barrier must be built up [1, 2]. The precise microstructural characteristics required to accomplish the varistor effect are still in debate [3–5], however, in a conventionally processed varistor not all the grain boundaries are useful [6].

The commercial formulations for ZnO based varistors include additions of Bi₂O₃, Sb₂O₃, MnO₂, Cr₂O₃ and Co₃O₄ [1, 2, 7–9]. Phases such as Zn₇Sb₂O₁₂ (with spinel structure) and Zn₂Bi₃Sb₃O₁₄ (with pyrochlore structure) formed during sintering, contribute to the formation of potential barriers at the grain boundaries [10, 11]. Therefore, to increase the amount of useful grain boundaries in between the electrodes, a microstructure with homogeneous distribution of these two phases is desirable. Although the

phases required in the microstructure are formed during sintering, the grain growth appears as a drawback. Reducing the grain size would increase the device breakdown voltage and enable the device miniaturization, just as the current electronic industry is demanding [12].

In the search for better processing techniques, mechanical activation looks as a good candidate for the fabrication of varistors. Mechanical activation can be achieved by using high energy milling of the mixture of reactants. There are several conventional milling devices such as the ball mill and the attritor which are not considered as high energy techniques [13]. High energy milling can be accomplished by using a shaker mill (SPEXTM) [13].

As in conventional milling processes particle size reduction and good homogeneity in the powder mixture can be accomplished by mechanical activation. Additionally, this technique allows allotropic transformations and the activation of chemical reactions [14–18]. Hence, chemical species or allotropic phases that

are thermally activated at high temperatures could be formed at room temperature.

Mechanical activation could be used to activate at room temperature, the phases required to accomplish the varistor effect and finally, to produce ZnO varistors with small grain size and good homogeneity in the microstructure.

In this work, the possibility of producing mechanical activation in the systems ZnO-Sb₂O₃ and ZnO-Sb₂O₃-Bi₂O₃ is explored.

2. Experimental Procedure

Commercial powders of ZnO (J. T. Baker, 0.5 μm), Sb₂O₃ (Aldrich, 0.8 μm), Bi₂O₃ (Aldrich, crystals of 50 μm long), were mixed in stoichiometric ratios corresponding to Zn₇Sb₂O₁₂ (spinel) and Zn₂Bi₃Sb₃O₁₄ (pyrochlore). The mixtures were milled up to 180 minutes in a shaker mill (SPEX model 8000-D) using stainless steel containers (3 cm diameter barrels) and milling media (0.5 cm diameter balls). The sample mass to milling media ratio was 1:10 [19]. Contamination of iron coming from the milling device was removed by a magnetic mixer. Both, the contamination and the final composition in the milled mixtures were determined by Atomic Absorption Spectrophotometry (Perkin Elmer AAnalyst 300). Iron contents were determined to be between 100 and 700 ppm. After milling, the mixtures were characterized by X-ray Diffraction (XRD) (Siemens 5000), Differential Thermal Analysis (DTA) (DTA-Setaram 2002) and Thermogravimetric Analysis (TGA) (TG-Setaram 2002). The mixture ZnO + 2.7 wt% Sb₂O₃ + 4.5 wt% Bi₂O₃ corresponding to a conventional formulation of varistors was also milled up to 180 minutes in a SPEX mill, isostatically pressed (Autoclave Engineering) at 300 MPa and sintered at 1200°C for 2 hours. After conventional polishing the sintered samples were chemically etched using 100 % acetic acid for 10 minutes. The microstructures of the sintered samples were observed by Scanning Electron Microscopy (SEM) (Jeol 6300). Disks of 1 cm of diameter and 1 mm thick, were cut from the sintered pieces. Silver was evaporated through a mask on the ceramic disks, leads were cold joined using silver paste and the whole device was covered with high resistivity epoxy resin (Eseisa MPT-M3, Mexico). I-V curves of the devices were obtained using an electrometer (Keithley 6517A) equipped with a D.C voltage source (0–100 V).

3. Results and Discussion

3.1. Spinel Composition

The XRD patterns of the unmilled and milled samples prepared with the mixture corresponding to the spinel phase, are shown in Fig. 1. The XRD peaks widen and their intensity decreases. As can be observed, only the ZnO and Sb₂O₃ phases are detected in all samples.

DTA and TGA curves for the unmilled and milled samples can be observed in Figs. 2 and 3 respectively. At least 5 thermal events are observed in Figs. 2 and 6 events in Fig. 3. No additional chemical reactions are produced by milling since the same number of events appear in all the samples. The weight loss occurring

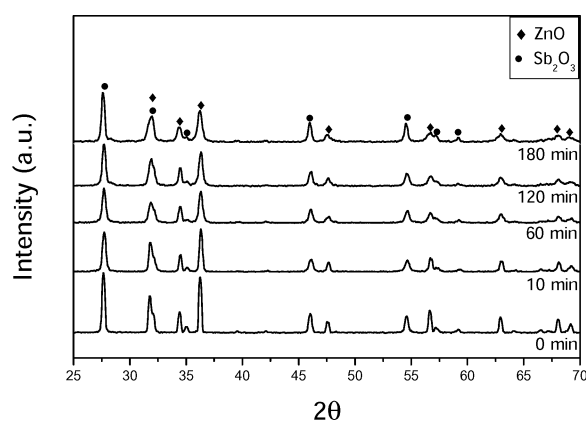


Fig. 1. XRD patterns of the unmilled and milled ZnO-Sb₂O₃ mixtures (spinel composition).

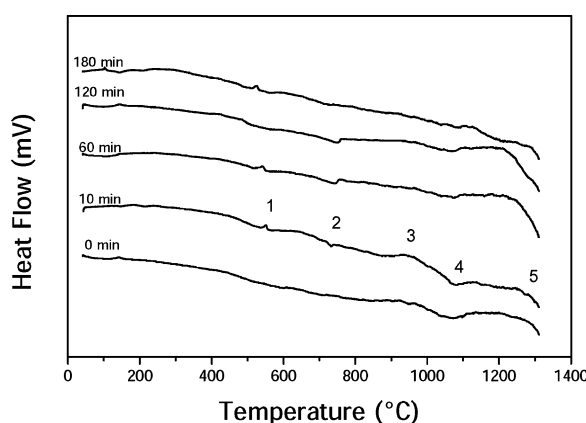


Fig. 2. DTA of the unmilled and milled ZnO-Sb₂O₃ mixtures (spinel composition).

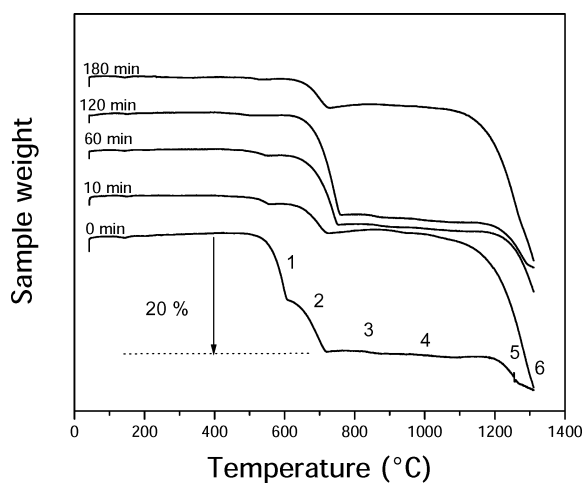


Fig. 3. TGA of the unmilled and milled ZnO-Sb₂O₃ mixtures (spinel composition).

between 400 and 800°C in the unmilled sample (Fig. 3) corresponds to ~20% of the total weight and it might be due to the volatilization of Sb₂O₃ [20].

Thermal events 3 (620°C), 4 (900°C) and 5 (1100°C) in Fig. 3, can be assigned to the formation of ZnSb₂O₆, Zn_{2.33}Sb_{0.67}O₄ and Zn₇Sb₂O₁₂ respectively. The formation of these compounds were reported [21] at around 800, 900 and 1100°C respectively, in samples with the same composition used in this work.

3.2. Pyrochlore Composition

In the case of the mixture ZnO-Bi₂O₃-Sb₂O₃, the effect of milling time can be observed in the XRD patterns presented in Fig. 4. For the sample milled during 60 minutes, the peak appearing at $2\theta = 28.2^\circ$, which does not appear neither in the unmilled sample nor in the sample milled for 10 minutes could correspond to the main peak of either rhombohedral Bi₂O₃ [22] or Bi₃SbO₇ [23]. At longer milling times the patterns show that the samples became amorphous.

In the DTA curve for the unmilled sample (Fig. 5), 4 thermal events are displayed. The same number of events have been reported by M. Inada and M. Matsuoka [24] using the same composition used in this work. They identified the events 3 and 4 in Fig. 5 (0 min), as corresponding to the pyrochlore and spinel formation respectively. In the same figure, the DTA curve for the sample milled for 180 minutes shows

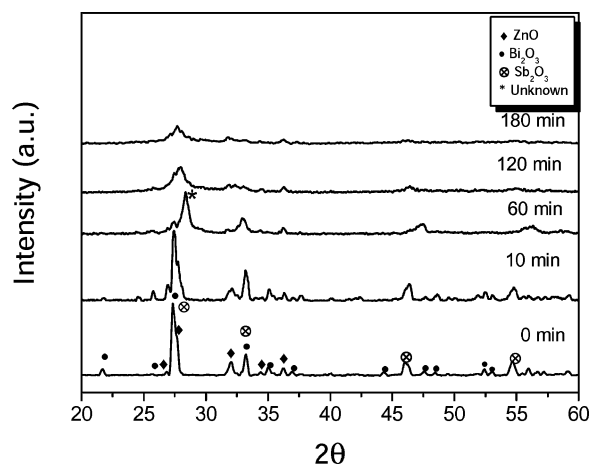


Fig. 4. XRD patterns of the unmilled and milled ZnO-Sb₂O₃-Bi₂O₃ mixtures (pyrochlore composition).

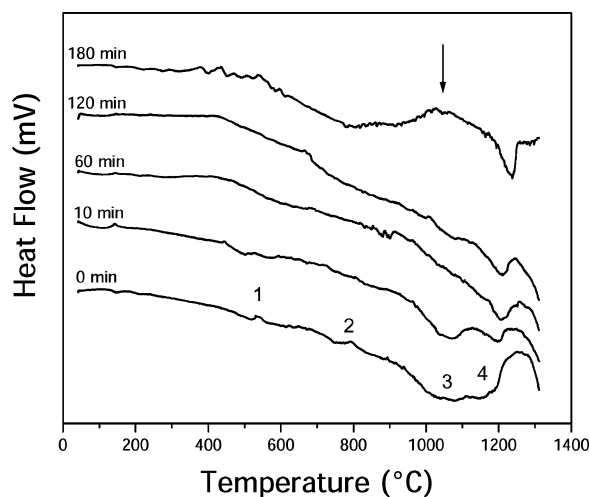


Fig. 5. DTA of the unmilled and milled ZnO-Sb₂O₃-Bi₂O₃ mixtures (pyrochlore composition).

an exothermic diffused event (pointed with an arrow) which could correspond to a recrystallization process.

In the Fig. 6, the weight loss occurring at ~600°C in the cases of the unmilled and the 10 minutes milled samples, does not occur in the samples milled for 60 minutes or longer. This event could correspond to the formation of Bi₃SbO₇ [23] which suggests that in the samples milled for 60 minutes or longer this compound has already been formed. Therefore, the XRD peak appearing at $2\theta = 28.2^\circ$ in the sample milled for 60 minutes should correspond to Bi₃SbO₇. Moreover,

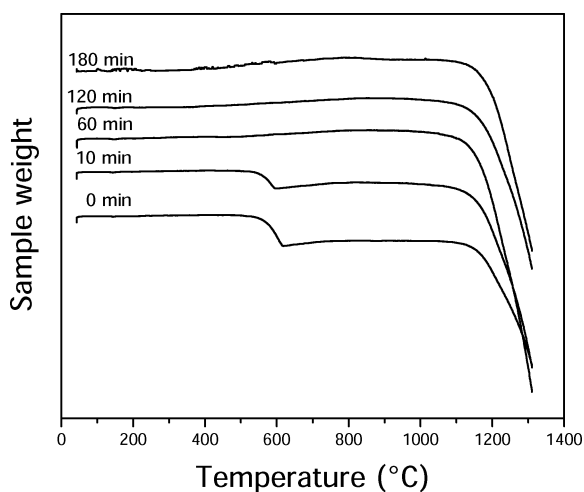


Fig. 6. TGA of the unmilled and milled ZnO-Sb₂O₃-Bi₂O₃ mixtures (pyrochlore composition).

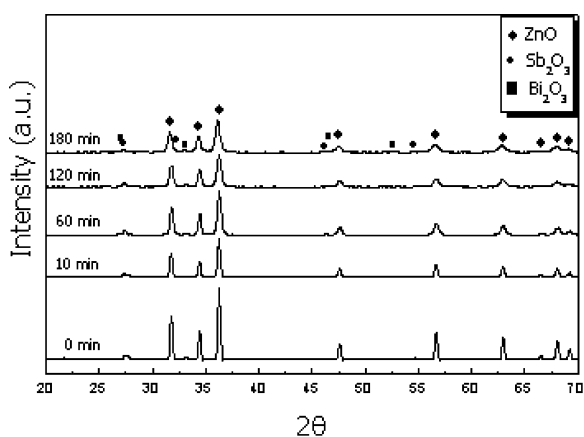
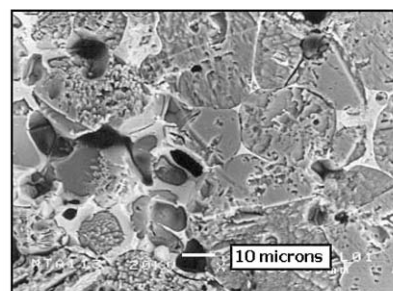


Fig. 7. XRD patterns of unmilled and milled ZnO + 2.7 wt% Sb₂O₃ + 4.5 wt% Bi₂O₃ mixtures (commercial composition).

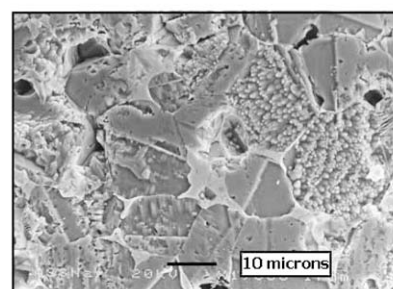
the peak at $2\theta = 27.5^\circ$ observed in the unmilled sample, is in fact a superposition of Bi₂O₃ and Sb₂O₃ peaks, and the intensity of both decreases remarkably after 60 minutes of milling. This suggests that both reactives are consumed to produce a new specie; namely Bi₃SbO₇.

3.3. Fabrication of Varistors

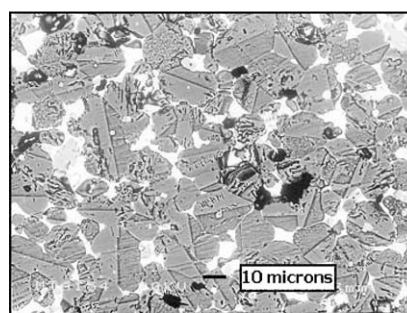
Varistor devices were fabricated using samples of the mixture ZnO + 2.7 wt% Sb₂O₃ + 4.5 wt% Bi₂O₃



(a)



(b)



(c)

Fig. 8. SEM micrographs of samples milled for (a) 0 minutes, (b) 60 minutes, and (c) 180 minutes, sintered at 1200°C for 2 hours (commercial composition).

milled up to 180 minutes to observe the effect of the mechanical activation on a commercial composition. The XRD patterns of the milled mixtures are presented in Fig. 7. Only the intensity reduction and widening of the XRD peaks are evident when the milling time is increased; no other phases different from those expected could be detected.

The microstructures of the samples milled during different times, isostatically pressed and sintered, are presented in Fig. 8. The twins and the sub-grain

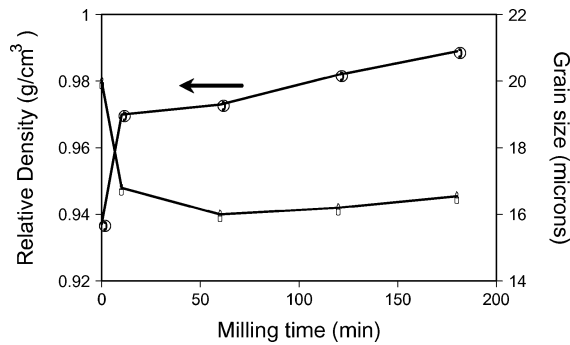


Fig. 9. Relative density and grain size as a function of the milling time for samples of the mixture ZnO + 2.7 wt% Sb₂O₃ + 4.5 wt% Bi₂O₃ (commercial composition) sintered at 1200°C for 2 hours.

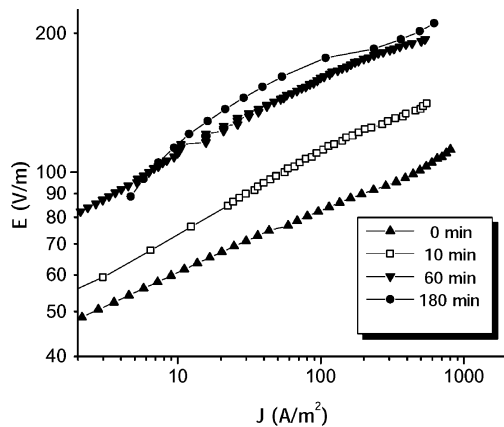


Fig. 10. Electrical field (E) as a function of the electrical current density (J) for samples of unmilled and milled ZnO + 2.7 wt% Sb₂O₃ + 4.5 wt% Bi₂O₃ (commercial composition) mixtures sintered at 1200°C for 2 hours. All the samples were 1 mm thick with a contact area of $7.85 \times 10^{-5} \text{ m}^2$.

boundaries observed in Fig. 8 are features commonly observed in ZnO varistor microstructures [25]. When the milling time increases, the density and the homogeneity of the grain size in the sintered samples improve, and the average grain size decreases slightly (Fig. 9). The devices fabricated with unmilled and milled powders display the typical non-Ohmic behavior (Fig. 10). In Table 1, $V_{1\text{mA}}$ is the breakdown voltage taken as the voltage measured when 1 mA is flowing through the device. $\alpha = d(\ln J)/d(E)$ is the nonlinearity coefficient. When the grain size is decreased an increment in the breakdown voltage is expected since there are more potential barriers between electrodes [1]. Not all the grain boundaries have the proper char-

Table 1. Breakdown voltage ($V_{1\text{mA}}$) and nonlinearity coefficient α for unmilled and milled powders sintered at 1200°C for 2 hours.

Milling time (min)	$V_{1\text{mA}}$	Average α
0	76	7.3
10	99	5.4
60	144	6.3
180	161	5.8

acteristics in order to obtain the varistor effect [3, 6], but a homogeneous dispersion of dopants could increment the number of grain boundaries with non-Ohmic characteristics. Hence, besides the grain size reduction, the milling process also provides good dispersion of the dopants in the final microstructure which would increment the breakdown voltage of the device. The values of α reported in literature [11] for varistors containing only Bi₂O₃ and Sb₂O₃ as dopants are in accordance with those values presented in Table 1.

4. Conclusions

A chemical reaction and amorphization can be mechanically activated in the system ZnO-Sb₂O₃-Bi₂O₃ by milling in a SPEX mill for 60 minutes or longer.

The weight loss due to volatilization that occurs in both ZnO-Sb₂O₃ and ZnO-Sb₂O₃-Bi₂O₃ systems at temperatures lower than 1200°C can be reduced by milling the powder mixtures.

Higher breakdown voltages are obtained when the milling time is incremented mainly because the grain size reduction and better homogeneity in the microstructure.

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