

## THE EFFECT OF THE PbO ADDITION ON THE SINTERING OF ZnO

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*The microstructural evolution and densification for the ZnO-PbO system were studied. Specimens were prepared by the mixed oxide route, and sintered at temperatures in the range of 1000-1300°C. The bulk densities of the PbO-added ZnO samples increased from 1000 to 1100°C. In sinterings above 1100°C, the bulk density was decreased almost linearly due to lead oxide evaporation except in 2.5 mol% PbO-added ZnO samples. The ZnO-PbO ceramics have a two phase microstructure comprising ZnO grains and a Pb-rich phase at the grain boundaries. The average grain size of ZnO increases with the PbO addition up to 7.5 mol% PbO addition but, the excess PbO addition decreases the grain size. This is due to the change in the grain growth mechanism from the solution precipitation in the liquid-phase to that of an ion diffusion mechanism in a thicker layer of liquid.*

## INTRODUCTION

ZnO based varistor ceramics have technological importance because of their highly non-linear electrical characteristics enabling them to be used as reversible, solid state switches with large energy-handling capabilities [1].

Commercial ZnO varistor ceramics are compositionally designed to contain several metal oxides, which modify the sintering and electrical properties of these ceramics, which show unique electrical properties. Additions may include Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CoO/Co<sub>3</sub>O<sub>4</sub>, MnO/MnO<sub>2</sub> and other oxides, each of which makes specific contribution to the microstructural evolution of the ZnO during sintering as well as to the electrical characteristics of the fired ZnO based ceramic varistor [2]. The electrical properties of these polycrystalline ceramics directly depend on the microstructure. For example, the grain size affects the varistor breakdown voltage per unit thickness. Other properties of polycrystalline ceramics also depend on the microstructure, so it is important in a general sense to fundamentally understand the microstructural development of ZnO ceramics [3]. Therefore, it is important to study in a systematic way the effect of these additives on the microstructural development.

Since the non-linearity is attributed to the grain boundary barriers, a two-phase microstructure (with the ZnO-rich grains forming the primary phase and the grain boundaries the second phase) is essential for non-linear ZnO [4]. Although numerous metal oxides are used as additives for ZnO ceramic varistors, Bi<sub>2</sub>O<sub>3</sub> is invariably present in the composition to enable liquid phase sintering and because it has been essential for imparting nonohmic behaviour to ZnO [5]. Bi<sub>2</sub>O<sub>3</sub> does not form any phase with ZnO. Hence in this work, PbO was considered as an alternative additive to Bi<sub>2</sub>O<sub>3</sub> due to its low melting (888°C) temperature [6]. For this reason the effect of PbO additions at 2.5, 5.0, 7.5 and 10 mol% on the sintering of ZnO was studied.

## EXPERIMENTAL

High-purity ZnO (>99.8%, Metal Bileşikleri A.Ş. Gebze, Kocaeli, Turkey) and PbO (Merck-pure grade) were used to prepare the compositions of ZnO with 2.5, 5.0, 7.5 and 10 mol% PbO. The calculated amounts of oxides for compositions were ball-milled in ashless rubber-lined jars for 3 hrs using zirconia balls and deionized water as milling media. After drying, the mixtures were granulated in moist conditions and semi-dry pressed at 50 MPa to prepare cylindrical specimens

12.5 mm in diameter and 10 mm in thick. The specimens were sintered at 1000, 1100, 1200 and 1300°C in air for 1, 2, 5 and 10 hrs, in a PID controlled SiC-furnace and cooled naturally.

The bulk densities of the sintered samples were determined from their weights and dimensions. The characterisation of sintered specimens was carried out by X-ray diffraction using CuK $\alpha$  radiation. For the microstructural observations both scanning electron microscopy (SEM) of the fracture surface and optical microscopy of polished and 20 % acetic acid-distilled water solution etched surfaces were used. The quantitative grain-size measurements were done on the micrographs of the samples using the following equation,

$$\bar{G} = 1.56 \bar{L} \quad (1)$$

where  $\bar{G}$  is the average grain size,  $\bar{L}$  is the average grain boundary intercept-length of random lines on two different micrographs for each sample [7].

## RESULTS AND DISCUSSION

### The effects of PbO on the densification

The bulk densities of the specimens with different PbO contents sintered at different temperatures for 1 hr are given in figure 1. The bulk densities of PbO-added ZnO samples increased with the increasing PbO content until 1100°C. When the sintering temperature was increased above 1100°C, the bulk densities of 5, 7.5 and 10 mol% PbO-added ZnO samples were lower than that of a 2.5 mol% PbO-added sample. Therefore, the volatility of PbO was investigated for the 2.5 and 10 mol% PbO-added ZnO compositions. The weight loss of these compositions was determined by weighing the green-pressed pellets before and after heating to the sintering temperatures by employing the same conditions used in sinterings. The weight loss data for these samples are given in table 1. The data at 1000°C indicates that 37 % of the PbO in the samples are lost. The PbO evaporation reached approximately 97 % at 1300°C. Hence, the densification observed in all samples up to 1100°C can be explained by the PbO liquid filling the cavities of the ZnO grains. Therefore, the evaporation of the excess liquid PbO does not affect the densification at this stage of the sintering but, above this temperature the increased rate of evaporation of PbO present as an excessive amount than the minimum level required for wetting the ZnO grains is reflected as a severe de-densification to the bulk density of the samples. The continuous increase in the bulk density of the sample containing 2.5 mol% PbO up to 1300°C can be attributed to the balance of the critical amount of the PbO liquid required to wet all the ZnO grains for enhancing the densification rate by solution and precipitation mechanism.

Table 1. The weight losses of PbO in the ZnO-PbO system.

compositions	sintering temperature			
	1000°C	1100°C	1200°C	1300°C
ZnO-2.5 mol% PbO	2.5 %	4.8 %	6.4 %	6.4 %
ZnO-10 mol% PbO	9.1 %	16.8 %	21.5 %	21.5 %

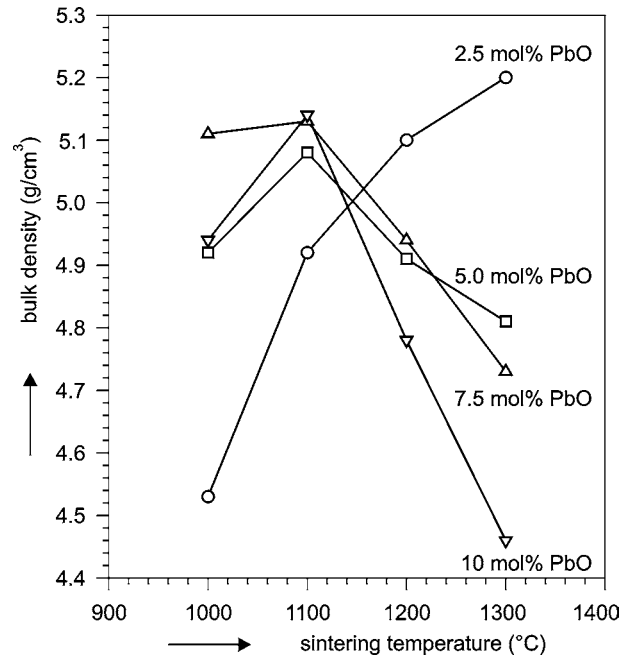


Figure 1. The bulk density vs. sintering temperature for PbO-added ZnO.

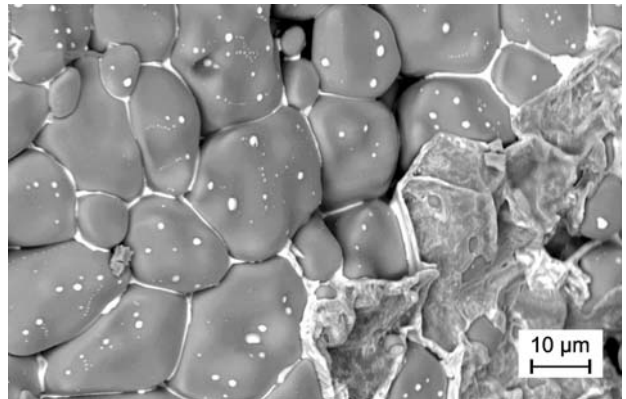


Figure 2. Backscattered electron SEM image of ZnO containing 5 mol% PbO sintered at 1300°C for 1 hr.

### The effects of PbO on the microstructure

The X-ray powder diffraction of the PbO-added ZnO samples sintered at different temperatures and different times showed the presence of ZnO (ASTM No: 36-1451) and PbO (ASTM No: 38-1477) as separate phases. PbO does not react with ZnO to form a phase as

indicated by the phase diagram of the ZnO-PbO binary system [8]. The backscattered electron images of the 5 mol% PbO-added ZnO sample sintered at 1300°C for 1 hr is given in figure 2. The micrograph clearly shows the PbO phase as bright regions between the ZnO grains. The bright spots on the ZnO grains reflects the PbO entrapment at the triple grain junctions.

The microstructures of the sintered surface for added ZnO samples with 2.5, 5, 7.5 and 10 mol % PbO sintered at 1300°C for 1 hr are shown in figure 3a-d. All the specimens have uniform grains, with some pores trapped in the grains and at triple grain junctions. The large cavities are due to pull-outs in the sample polishing process. The relationship between the average grain size and the level of PbO-doping for the samples sintered at 1100 and 1300°C for 1 hr is given in figure 4. As it is seen in this figure, the average grain size of undoped ZnO is about 4  $\mu\text{m}$  at 1100°C for 1hr sintering and about 10  $\mu\text{m}$  at 1300°C for 1hr [9]. Also, the average grain size of ZnO increases with the PbO addition to the 7.5 mol% PbO addition level. In the case of the

10 mol% PbO addition, the average grain size decreases. The numerous studies carried out on the grain growth of ZnO have revealed that the rate-controlling mechanism is the solid state diffusion of Zn<sup>2+</sup> cations[10] but, in ZnO with the PbO additions, the liquid phase sintering controls the grain growth. In the ZnO-PbO ceramics system, ZnO dissolves up to 5 mol% in PbO[8]. Hence, the quantity of ZnO to be dissolved in PbO increases with the PbO content. The grain growth of ZnO proceeds in the PbO liquid phase by a mechanism of solution-precipitation at phase boundaries up to 7.5 mol% PbO, but in the higher PbO content level this mechanism is replaced by the diffusion of Zn<sup>2+</sup> ions through the thicker layer of liquid. Therefore, the greater the amount of liquid phase, the larger diffusion distance and the lower rate of ZnO grain growth occurs [5]. It is concluded that, the rate-controlling mechanism for the grain growth of ZnO changes from phase-boundary reaction control in the PbO content from 2.5-7.5 mol% to the diffusion through the PbO rich liquid phase at the higher PbO content.

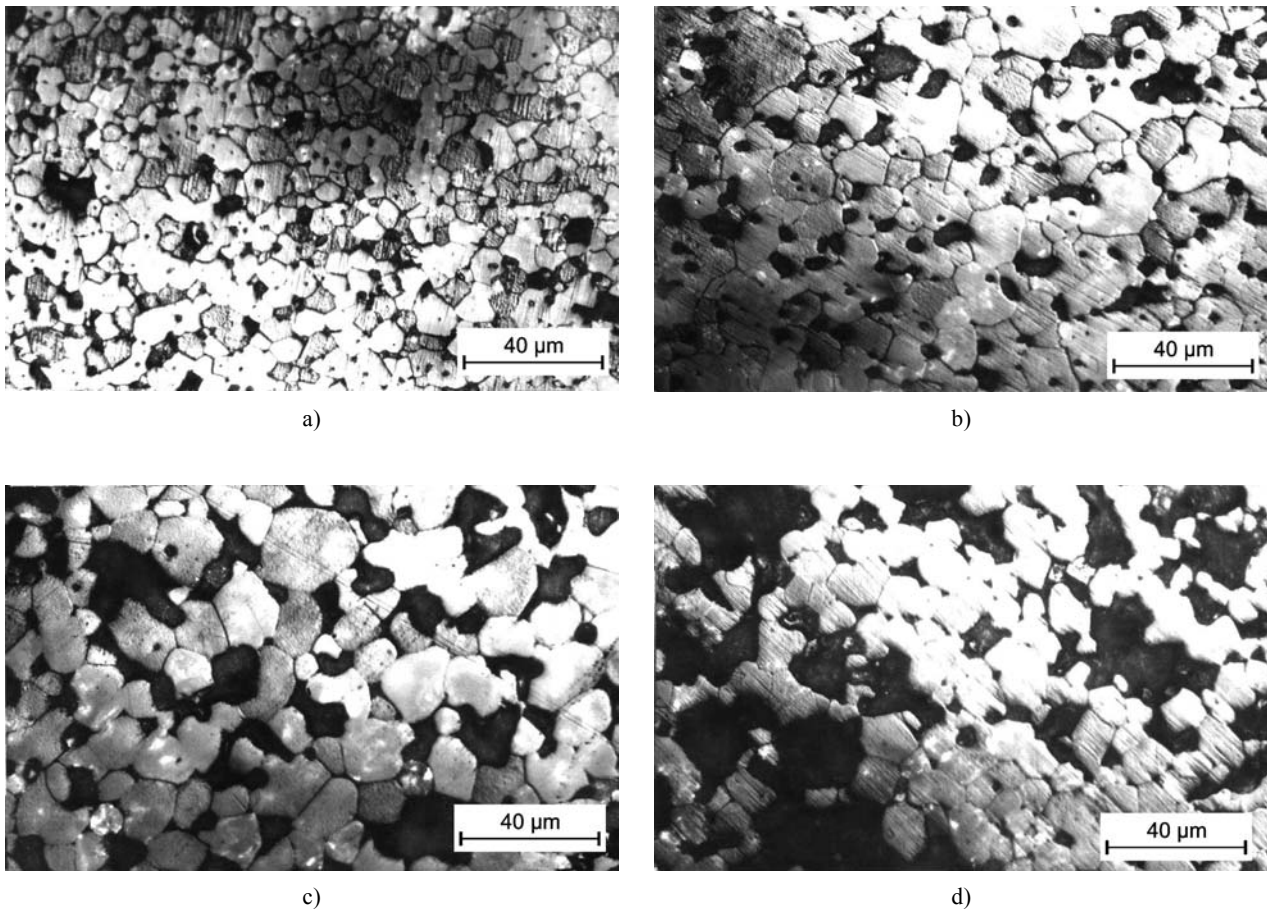


Figure 3. Microstructures of ZnO containing (a) 2.5, (b) 5.0, (c) 7.5 and (d) 10 mol% PbO sintered at 1300°C for 1 hr.

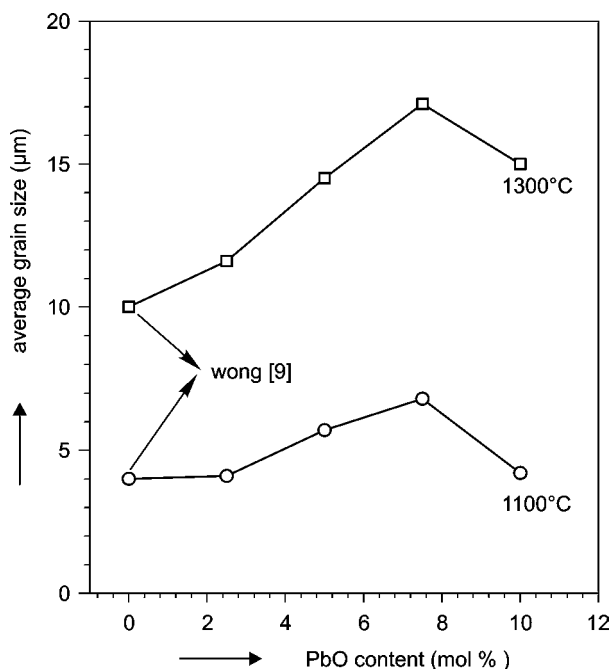


Figure 4. The relationships between the average grain size and PbO content for samples sintered at 1100 and 1300°C for 1 hr.

#### CONCLUSION

The microstructure of ZnO during the liquid phase sintering in the binary ZnO-PbO system with 2.5, 5.0, 7.5 and 10 mol% PbO was studied. The bulk densities of PbO-added ZnO samples increased from 1000 to 1100°C. In sinterings above 1100°C, the bulk density was decreased almost linearly due to lead oxide evaporation except in the 2.5 mol% PbO-added ZnO samples. The ZnO-PbO ceramics have a two-phase microstructure comprising ZnO grains and a Pb-rich phase at the grain boundaries. The average grain size of ZnO increases with a PbO addition up to 7.5 mol%, but excess above this level decreases the grain size. This is due to the change in the grain-growth mechanism from the solution precipitation in the liquid-phase to that of an ion diffusion mechanism in a thicker layer of liquid.

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#### VLIV PŘÍDAVKU PbO NA SINTROVÁNÍ ZnO

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Byl studován vývoj mikrostruktury a zhutňování v systému PbO-ZnO. Vzorky byly připraveny smícháním oxidů a sintrovány v teplotním rozmezí 1000-1300°C. Objemové hustoty ZnO s přidavkem PbO rostly mezi 1000 a 1100°C. Při sintrování nad 1100°C klesala objemová hustota skoro lineárně díky odpařování PbO s výjimkou vzorku ZnO s 2,5 mol% PbO. Keramiky ZnO-PbO měly dvoufázovou mikrostrukturu se zrn ZnO a Pb-bohatou fází na rozhraní zrn. Průměrná velikost zrn ZnO roste s přidavkem PbO až do 7,5 mol%, ale další přebytek PbO velikost zrn snižuje. Je to způsobeno změnou mechanismu růstu zrn od srážení z roztoku v kapalné fázi k iontové difúzi v tlustší vrstvě kapaliny.