THE INFLUENCE OF Sb_2O_3 PROPORTION ON THE ZnO GRAINS GROWTH DURING SINTERING

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Mărimea grăunților de ZnO influențează caracteristicile V-I şi celelalte proprietăți electrice ale rezistorilor neliniari de ZnO. În prezenta lucrare se evidențiază influența proporțiilor de Sb_2O_3 asupra creşterii grăunților de ZnO în condiții diferite de sinterizare (temperatura şi durata variabile). Adaosurile de Sb_2O_3 determină o scădere a creşterii grăunților, pentru toate compozițiile ZnO-Sb_2O_3 ca urmare a apariției fazei cristaline de spinel şi a prezenței maclelor, limita de grăunte suferind o reducere de mobilitate ca urmare a unui mecanism de blocare.

The ZnO non-linear resistors V-I characteristics and other electrical properties are influenced by the ZnO grain size. In the present paper the influence if the Sb_2O_3 amount on the ZnO grain growth is evidenced for different sintering conditions (varying temperature and time). For all the ZnO- Sb_2O_3 compositions, the Sb_2O_3 additions determine a decrease of the grain growth, as a consequence of the spinel crystalline phase appearance and of the twin presence, the grain boundary suffering a mobility reduction due to a blocking mechanism.

Keywords: twinning, sintering, ZnO grains, Sb_2O_3

1. Introduction

Nonlinear VI characteristics of ZnO resistors and electrical properties are influenced by grain size of ZnO, the ceramics microstructure, density and thickness of ceramic structures. These last ones are influenced by variables of the process and introduced oxide additions [1-3].

Metal oxides such as Bi_2O_3, Sb_2O_3, MnO_2, Cr_2O_3, CoO, etc., are present in all of ZnO non-ohmic ceramics. These oxides melt at low temperatures 825°C (Bi_2O_3) and 665°C (Sb_2O_3), respectively, allowing the sintering in presence of a liquid phase. The liquid phase helps the ceramic densification and determines the non-ohmic behavior of zinc oxide ceramic. After sintering process, the ZnO non-

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ohmic ceramic contains the following crystalline phases: ZnO grains doped with Co and Mn; small spinel particles $Zn_7Me_2O_{12}$ (Me = Sb, Cr, Mn, Co) formed at grains boundaries, thus being the intergrain phase; pyrochlore phase $Bi_2(Zn_{4/3}Sb_{2/3})O_6$ with doping elements such Co, Cr and Mn, and bismuth rich phase containing doping elements Zn and Sb [3-5].

Newly formed spinel particles reduce the growth rate of ZnO grains by a blocking mechanism [5-6].

2. Experimental

The mixtures from ZnO were obtained and addition oxide in proportions of 0.3%, 0.6%, 1.2% and 2.4% Sb_2O_3 (% wt). The used oxides (ZnO and Sb_2O_3) were chemically pure.

The average grain size of used zinc oxide was 18.5μm. The grain size distribution of used ZnO is presented in Fig. 1.

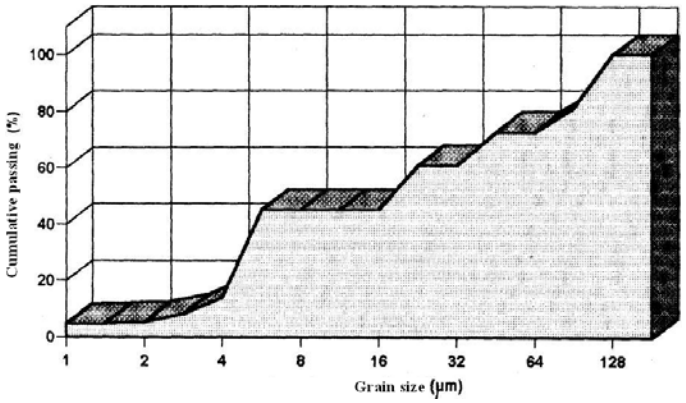


Fig.1 The grain size distribution of ZnO

The powders were mixed in a ball mill for samples preparation. Polyvinyl alcohol 3%wt was used for binding. The mixtures were uniaxial pressed into metallic mould with a 60MPa.

Disks with 16.82 mm diameter and variable heights (between 1 and 4 mm) were obtained. The samples were thermally treated in air at 500°C for 0.5 hours, for binder burning. After that, the samples were sintered at 1100°C, 1200°C, 1300°C and 1400°C. The soaking time was varied from 0.5 hour to 16 hours.

The obtained samples were analyzed as density, and microstructure.

The sample density was determined by the Archimedes method, and the microstructural analyses were made with a SEM 515 Philips scanning electron microscope.

The relative intensities of the characteristic X-rays of the compositions were obtained using a D8 ADVANCE type X-ray diffractometer (technical

features: Cu and Mo anode X-ray tubes; vertical goniometer; scanning θ-2θ, or θ or 2θ, minimum step 2θ=0,0001; maximum scanning rate =25%). The apparatus allowed a qualitative analysis of the polycrystalline materials; the determination of the average size of the crystallites as well as of the elementary cell parameters.

3. Results and discussions

3.1. Samples densities

The density values for untreated and sintered samples were determined by measurements made on lots of 4 pieces, obtained under similar conditions.

The results obtained for untreated samples are presented in Table 1. Sintering conditions and the results obtained for sintered samples are presented in Table 2.

Table 1

Density values for the untreated samples

No.	Mixture	Density for untreated samples (g/cm^3)
1	$ZnO+0.3\%Sb_2O_3$	3.48
2	$ZnO+0.6\%Sb_2O_3$	3.49
3	$ZnO+1.2\%Sb_2O_3$	3.53
4	$ZnO+2.4\%Sb_2O_3$	3.58

Table 2

Working conditions and density values for the sintered samples

Composition	Temperature (°C)	Soaking time (h)	Apparent density (g/cm^3)
$ZnO+0.3\%Sb_2O_3$	1100	2	5.47
		8	5.45
		16	5.50
	1200	1	5.40
		2	5.49
		8	5.51
	1300	1	5.30
		2	5.52
		4	5.54
		8	5.55
	1400	0.5	5.32
		1	5.33
		2	5.35
		4	5.40
$ZnO+0.6\%Sb_2O_3$	1100	2	5.24
		8	5.32
		16	5.51
	1200	1	5.48
		2	5.50
		8	5.52
	1300	1	5.51
		2	5.53
		4	5.53

Composition	Temperature (°C)	Soaking time (h)	Apparent density (g/cm^3)
		8	5.34
	1400	0.5	5.38
		1	5.40
		2	5.42
		4	5.45
$ZnO+1.2\%Sb_2O_3$	1100	2	5.04
		8	5.44
		16	5.52
	1200	1	5.51
		2	5.52
		8	5.53
	1300	1	5.51
		2	5.53
		4	5.52
		8	5.48
	1400	0.5	5.50
		1	5.54
		2	5.52
		4	5.42
$ZnO+2.4\%Sb_2O_3$	1100	2	4.53
		8	4.82
		16	4.89
	1200	1	5.52
		2	5.53
		8	5.54
	1300	1	5.52
		2	5.54
		4	5.54
		8	5.54
	1400	0.5	5.51
		1	5.55
		2	5.50
		4	5.48

For a better observation, the density values are plotted in Fig. 1 for samples containing 1.2% Sb_2O_3, depending on soaking time.

The temperature has a favorable influence on the densification process.

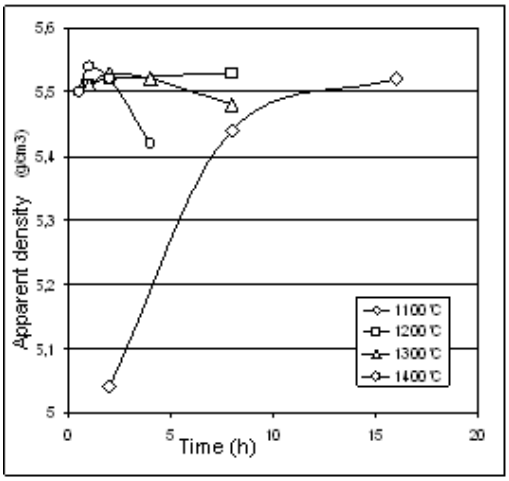


Fig. 1. Density evolution in time for samples containing 1.2% Sb_2O_3

The increase of the soaking time induces a good influence only for samples sintered at low temperatures (1100°C and 1200°C). The increase of the sintering temperature to 1300°C and 1400°C and the increase of soaking time, induce the decrease of density values, due to the emergence of the creep phenomenon initiated by the increase of the liquid phase amount occurred at sintering.

Fig. 2 shows the effects induced by the increase of the Sb_2O_3 proportion on the apparent densities of sintered samples, considering all the three conditions of sintering corresponding to different densification stages, namely: the low degree of sintering (2h/1100 C), the maximum degree of sintering (8h/1200°C), and the density decrease (4h/1400°C).

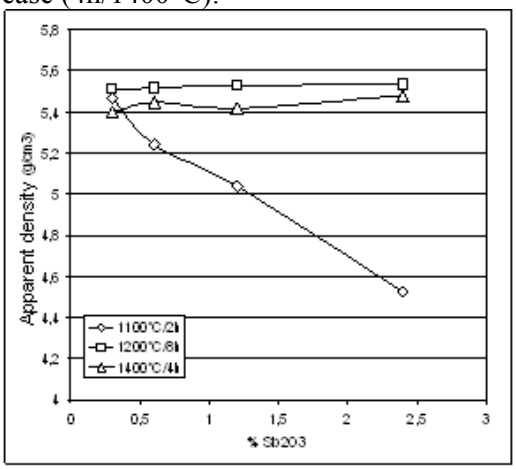


Fig. 2. Evolution as a function of Sb_2O_3 proportion

In the sintering conditions which induce low apparent density values (1100°C/2h), the apparent densities of ZnO-Sb_2O_3 ceramics linearly decrease with the increase of Sb_2O_3 proportion. This is due to the increased liquid amount formed at sintering, and it increases with the addition proportion.

For samples sintered at 1100°C/2h it is to be noted that the apparent density reaches maximal values, which slightly increased with Sb_2O_3 content, even if the theoretical density of Sb_2O_3 (5.2 g/cm^3) is lower than that of pure ZnO (5.61 g/cm^3). In this case, the densification process appears to be ended for all compositions.

The ceramics with high content of Sb_2O_3 sintered at 1200°C/8 h have highest densities. The results obtained could explain that the additions of Sb_2O_3 may reduce the decrease of density values.

3.2. X-ray diffractions in the ZnO- Sb_2O_3 system

Fig. 3-6 present the XRD patterns from 4 previously obtained ceramic samples: ZnO+0,3%Sb_2O_3 sintered at 1200°C for 8h; ZnO+0,3%Sb_2O_3 sintered at 1300°C for 8h; ZnO+1,2% Sb_2O_3 sintered at 1300°C for 8h; ZnO+1,2%Sb_2O_3 sintered at 1400°C for 4h.

The spinel formation is noticed in all the samples, and the spinel amount is higher when the antimony oxide and temperature and time of the heat treatment

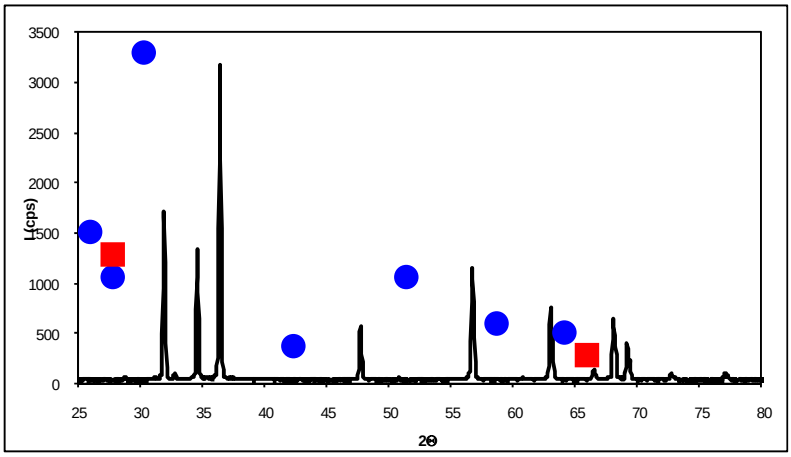


Fig. 3. X-ray diffraction pattern for the ZnO+0,3%Sb_2O_3 sample (at 1200°C/8h)
● ZnO (zincite), ■ spinnel $Zn_7Sb_2O_{12}$

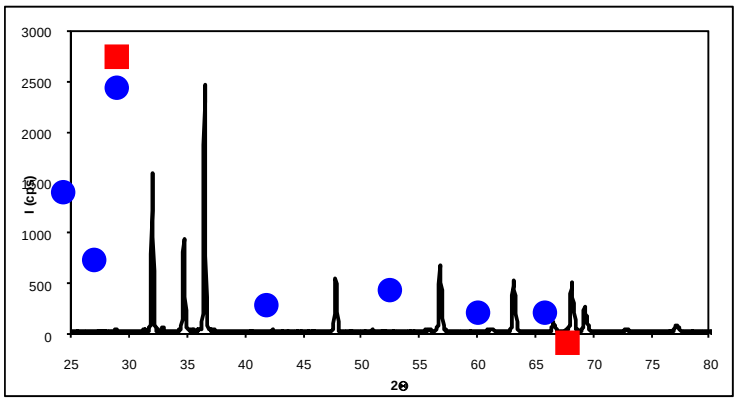


Fig. 4. X-ray diffraction pattern for the ZnO+0,3%Sb_2O_3 sample (at 1300°C/8h)
● ZnO (zincite), ■ spinnel $Zn_7Sb_2O_{12}$

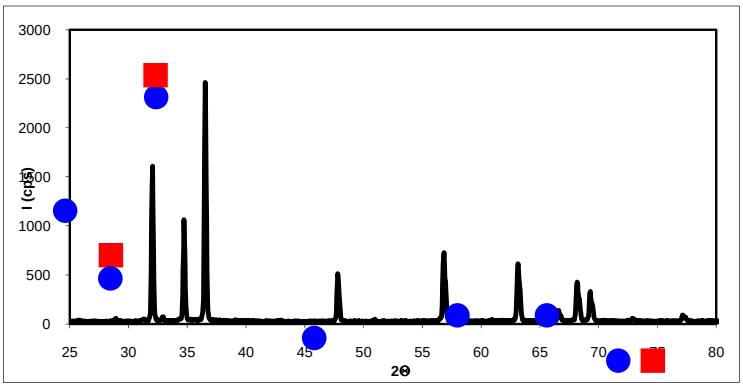


Fig. 5. X-ray diffraction pattern for the ZnO+1,2%Sb_2O_3 sample (at1300°C/8h)
● ZnO (zincite) , ■ spinnel $Zn_7Sb_2O_{12}$

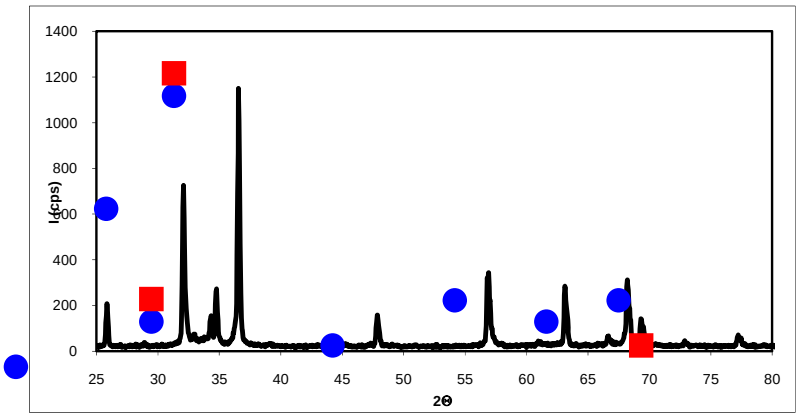


Fig. 6. X-ray diffraction pattern for the ZnO+1,2%Sb_2O_3 sample (at 1400°C/4h)
● ZnO (zincite) , ■ spinnel $Zn_7Sb_2O_{12}$

3.3. Microstructure of ZnO- Sb_2O_3 ceramic

Fine grains for ceramics with high Sb_2O_3 content are observed in Figs. 7-12, regardless of sintering condition.

The additions of Sb_2O_3 cause a decrease in grain growth for all compositions ZnO-Sb_2O_3. The $Zn_7Sb_2O_{12}$ spinel formation is due to reaction between Sb_2O_3 and ZnO during sintering.

The grain size of ZnO is supposed to be related to the presence of spinel grains. The inhibition mechanism of grain growth is probably the one which fixes the grain boundary or cleanes the spinel inclusions. The twinning presence is another aspect of ZnO-Sb_2O_3 compositions. The grain boundary which is coupled with a twinning structural limit may suffer a reduction in mobility. From this perspective, the twinning presence in grains can be considered as having an inhibitory effect on ZnO grain growth.

For samples ZnO+0.3% and 1.2%Sb_2O_3 sintered 1h at 1100°C and 1200°C and 8h at 1300°C, the surfaces fracture shows the temperature influence on the microstructure of these ceramics. Thus, the grains size and morphology was pointed out in Figs. 7-12. ZnO+0.3% and ZnO+1.2%Sb_2O_3 ceramics sintered 1h at 1100°C reveal a very low sintering degree. The material looks like a fine compact powder (≈1μm) without reaction between grains followed by a new phase formation (Fig. 7.8).

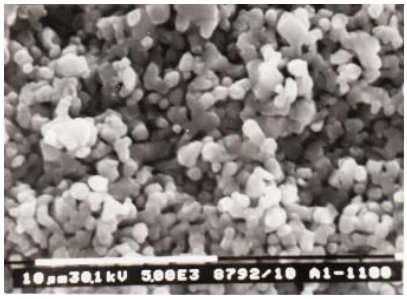


Fig. 7. Image of ZnO+0.3%Sb_2O_3 ceramic sintered 1h at 1100°C (x 5000)

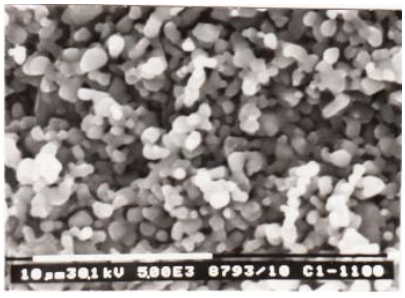


Fig. 8. Image of ZnO+1.2%Sb_2O_3 ceramic sintered 8h at 1100°C (x 5000)

Same materials sintered at 1200°C emphasize a progress of the sintering process due to the presence of bridges between particles, closed spherical pores and a more regular morphology of grains (close to polyhedral) – Fig. 9, 10.

Ceramics with coarse microstructures were obtained after sintering at 1300°C/8h. This demonstrates the influence of the temperature and soaking time increase on the promotion of the grain growth process (Figs. 11, 12).

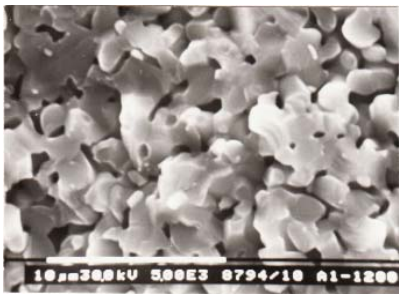


Fig. 9. Image of ZnO+0.3%Sb_2O_3 ceramic sintered 1h at 1200°C (x 5000)

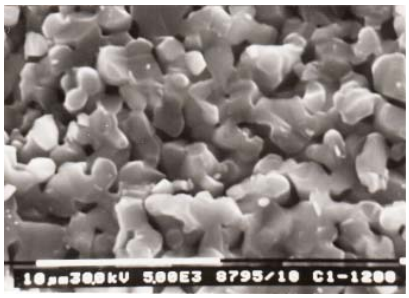
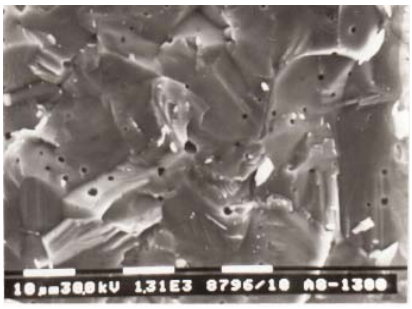
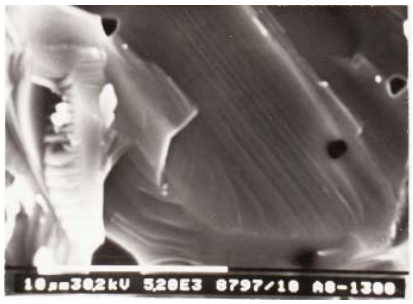


Fig. 10. Image of ZnO+1.2%Sb_2O_3 ceramic sintered 8h at 1200°C (x 5000)



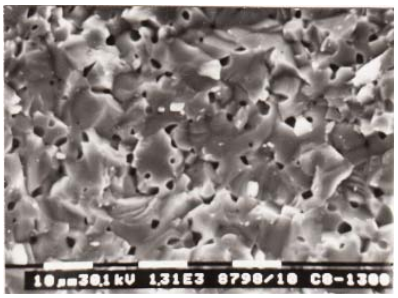
a) x 1310



b) x 5200

Fig. 11. Image of ZnO+0.3%Sb_2O_3 ceramics sintered 8h at 1300°C: (a) compact grains, closed spherical pores; (b) very fine twinning on grains surface

At higher magnification, the grains surface is seen to be streaked of very fine lines that are twinning (here the electrons have different tunnelling, depending on crystallographic orientation).



a) x 1310

b) x 5200

Fig. 12. Image of ZnO+1.2%Sb_2O_3 ceramic sintered 8h at 1300°C: (a) compact grains, closed spherical pores; (b) very fine twinning on grains surface

4. Conclusion

During sintering, the Sb_2O_3 additions on ZnO grains growth decrease the grains growth. The $Zn_7Sb_2O_{12}$ spinel particles are observed at grains boundary.

The Sb_2O_3 additions caused the twinning formation on each ZnO grain. The spinel particles and twinning could be responsible for inhibiting the grain growth of ZnO by a blocking mechanism.

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