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PHASE FORMATION MECHANISM IN THE ZnO-SnO_2 BINARY SYSTEM

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The Sn-Zn-O ceramics are very interesting materials for their applications as varistors, electrodes, catalysts and gas sensors. The present work deals with phase formations studies in the SnO_2-ZnO binary system over the whole concentration range. High-temperature interactions of the samples thermally treated in the 1000-1500ºC domain were evaluated by XRD and FT-IR Spectroscopy. Besides SnO_2 and ZnO only Zn_2SnO_4 ternary compound was found in our experimental conditions.

INTRODUCTION

The interest for ZnO and SnO_2 oxides is very high due to their specific semiconducting properties that make them suitable for different applications, as varistors,[1] thermoelectric materials with high-energy conversion efficiency,[2] gas sensors.[3] Nowadays, commercial ZnO–based varistors are produced with minor additions of typically Bi_2O_3, Sb_2O_3, CoO, MnO_2 and Cr_2O_3.[4] Gas sensing property of SnO_2-based ceramics was improved by addition of different additives,[5] while modified SnO_2 anodes have been used for the degradation of phenolic compounds[6] or in electrowining proceses.[7]

Literature data reported the formation of two compounds in the ZnO-SnO_2 system, namely zinc orthostannate with formula Zn_2SnO_4 and zinc metastannate, $ZnSnO_3$, respectively.

Mixtures of ZnO and SnO_2 powders with 2:1 molar ratio exhibit photocatalytic performance for methyl orange degradation.[8] Ceramic varistors with extensive regions of Zn_2SnO_4 have been obtained by Anastasiou *et al*.[9]

Literature data indicate that the formation temperature of the Zn_2SnO_4 compound strongly depends on the preparation method.[8, 10-12]

The formation of $ZnSnO_3$ is still ambiguous and contradictory. Shen and Zhang[13] reported a pure $ZnSnO_3$ phase with a perovskite-type structure which can be obtained only by a co-precipitation method using together oxalic acid and ammonia as precipitants. Kovacheva and Petrov[14] however showed that $ZnSnO_3$ can not adopt a perovskite structure under normal conditions, since the ionic radius of Zn^{2+} is too small. They succeeded to prepare $ZnSnO_3$ with an ilmenite-type structure by an ion-exchange reaction between Li_2SnO_3 and a melt of $ZnCl_2$-KCl. New type of $ZnSnO_3$ based varistor was obtained by Zang *et al*.[15] at 1427ºC, in pressed pellets at 160 MP. Zinc metastannate exhibits a limited thermal stability and in bulk samples its decomposition to Zn_2SnO_4 and SnO_2 has been noted at temperatures as low as 600 ºC.[16] A polar $ZnSnO_3$ oxide with a $LiNbO_3$-type structure (LN) was synthesized by solid state reaction at 1000 ºC under a pressure of 7 GPa[17] and the authors affirm that $ZnSnO_3$ is stable up to 700 ºC.

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Based on the serious discrepancies, that can still be found in the literature regarding the thermal evolution of the ZnO–SnO_2 binary system; in the present work a systematic study of the phase formation over the whole compositional range of the ZnO-SnO_2 binary system in the 500-1500 ºC temperature domain was approached.

EXPERIMENTAL

Mixtures of SnO_2 (Merck - reagent grade) and ZnO (Merck - reagent grade) powders with grain size up to 60 μm were wet homogenized during 15 minutes in the agate mortar in absolute ethanol. Initial molar compositions of the oxide mixtures, labeled 1-16 SZO, are shown in the Table 1.

Cylindrical samples with Φ=10 mm and h=2-3 mm were obtained by pressing at 100 MPa. The sample of (1-16) SZO, were calcined in a Nabertherm type oven at 500, 600, 800, 850, 900 and 1000ºC for 10 hours. The CARBOLITE HTF 1700 furnace was used for thermal treatment at higher temperatures, namely, at 1100, 1150, 1200, 1300, 1500ºC. After thermal treatment, all samples were cooled to room temperature with the furnace.

DTA and TG/DTG investigations were performed with a Mettler Toledo Derivatograph in the 20-1500˚C temperature range with a heating rate of 5˚C/min.

X-ray analysis of the obtained calcined samples was performed using a Rigaku Ultima IV diffractometer with Cu Kα radiation, with the scan step of 0.02º and scan speed of 5º/min. For XRD analyses following PDF Cards were used: SnO_2 01-071-0652; ZnO 00-036-1451; Zn_2SnO_4 00-024-1470; $ZnSnO_3$ 01-089-0095.

Room temperature infrared transmission measurements (FT-IR spectra) on the thermally treated samples were made with a Nicolet 6700 apparatus in 400-4000 cm^{-1} range. The spectra were taken from thin transparent (~20 mg/cm^2) KBr pellets containing approximately 0.5% wt samples. Pellets were prepared by compacting and vacuum-pressing an intimate mixture obtained by grinding 1 mg of substance in 200 mg KBr.

The microstructure of the samples was observed by Scanning Electron Microscopy (SEM FEI Quanta 200 type).

RESULTS

1. Phase formation in non-isothermal conditions

X-Ray diffractions patterns of SnO_2 and ZnO starting oxides are presented in Fig. 1. In the case of SnO_2 its rutile structure is confirmed (PDF Card: 01-071-0652) while in the case of ZnO the wurtzite structure was identified (PDF Card: 00-036-1451).

In order to establish the high temperature interaction in the ZnO-SnO_2 binary mixtures, in non-isothermal conditions, the thermal analysis curves have been recorded up to 1500ºC for the following samples: 1SZO (pure SnO_2), 8SZO (with SnO_2:ZnO=1:1 molar ratio)), 10SZO (with SnO_2:ZnO=1:2 molar rario) and 16SZO (pure ZnO). No thermal effects were observed on the DTA curves of the investigated samples indicating a continuously occurring interaction between the two components and not one at a given temperature represented by a definite thermal effect.

In Fig. 2 the XRD pattern of DTA residue of 8SZO sample is presented, showing the presence of the diffraction lines corresponding to a mixture of Zn_2SnO_4 and SnO_2. The obtained result indicates that in non-isothermal conditions the formation of $ZnSnO_3$ did not occur.

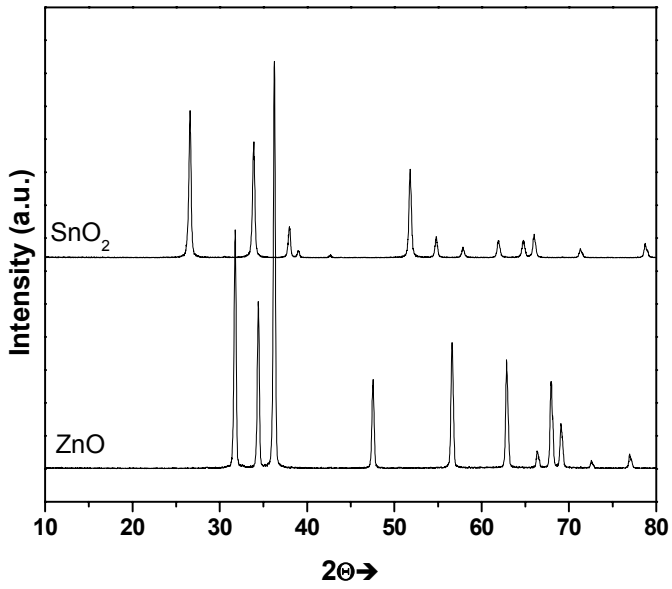

Fig. 1 – XRD patterns of the starting oxides.

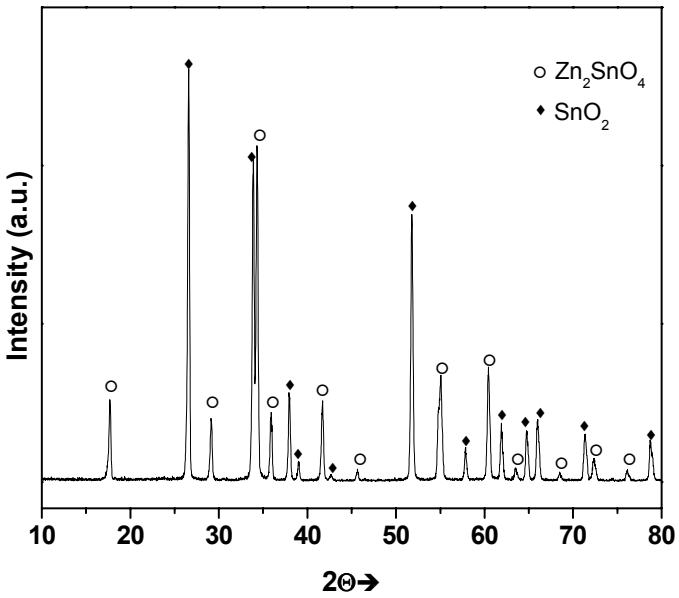

Fig. 2 – XRD pattern of DTA residue for 8SZO sample.

2. Phase formation in isothermal conditions

Considering literature data regarding the formation of different phases of interest in the studied system and based on the results obtained in non-isothermal conditions, all prepared samples (labeled 1-16 SZO) were thermally treated for ten hours at 500, 600, 800, 850, 900, 1000, 1100, 1150, 1300, 1400 and 1500 ºC temperatures, as mentioned above.

In Table 1 initial composition and phase composition at representative temperatures of thermal treatment for all samples are shown, while in Figs. 3 and 4 XRD patterns for some selected samples thermally treated at 1300 ºC are presented.

Up to 900 ºC only tetragonal SnO_2 and trigonal ZnO phases were identified by XRD analysis.

At 900 ºC for the 4-12 SZO samples, beside SnO_2 and ZnO, the presence of Zn_2SnO_4 inverse spinel was emphasized.

At temperatures ≥ 1000 ºC for the sample 10SZO (with SnO_2/ZnO=1:2 molar ratio) the pure spinel Zn_2SnO_4 phase was identified. In the case of 8SZO sample (with SnO_2/ZnO=1:1 molar ratio), in the same temperature range the formation of corresponding $ZnSnO_3$ was not identified, but the XRD characteristic lines of the mixture of SnO_2 and Zn_2SnO_4 phase (with the highest intensity belonging to Zn_2SnO_4) are detected.

For the samples 2SZO-9SZO mixtures of SnO_2 and Zn_2SnO_4 phases were obtained, while for the samples 11SZO-15SZO a mixture of ZnO and Zn_2SnO_4 was observed. An interesting behavior was noticed for the samples 2SZO and 15SZO, namely, for the sample 2SZO (with 97.5 mol % SnO_2) the diffraction lines assigned to Zn_2SnO_4 have a lower intensity then those obtained for the 15SZO sample (2.5 mol% SnO_2).

At 1400 and 1500 ºC no changes of the phase composition of the samples thermally treated at 1300 ºC were observed.

Table 1

Phase composition of the studied samples thermally treated at different temperatures

Samples	Initial composition (mol.%)		Phase composition			
	SnO_2	ZnO	500ºC	900ºC	1000ºC	1300ºC
1 SZO	100.0	0	SnO_2	SnO_2	SnO_2	SnO_2
2 SZO	97.5	2.5	SnO_2 ,ZnO	SnO_2 ,ZnO	SnO_2 , Zn_2SnO_4	SnO_{2ss}, Zn_2SnO_4
3 SZO	95.0	5.0	SnO_2 ,ZnO	SnO_2, ZnO	SnO_2 , Zn_2SnO_4	SnO_2 , Zn_2SnO_4
4 SZO	90.0	10.0	SnO_2, ZnO	SnO_2 , Zn_2SnO_4, ZnO	SnO_2 , Zn_2SnO_4	SnO_2 , Zn_2SnO_4
5 SZO	80.0	20.0	SnO_2, ZnO	SnO_2 , Zn_2SnO_4, ZnO	SnO_2 , Zn_2SnO_4	SnO_2 , Zn_2SnO_4

Table 1 (continued)

6 SZO	70.0	30.0	SnO_2, ZnO	SnO_2 , Zn_2SnO_4, ZnO	SnO_2 , Zn_2SnO_4	SnO_2 , Zn_2SnO_4
7 SZO	60.0	40.0	SnO_2, ZnO	SnO_2 , Zn_2SnO_4, ZnO	SnO_2 , Zn_2SnO_4	SnO_2 , Zn_2SnO_4
8 SZO	50.0	50.0	SnO_2, ZnO	SnO_2 , Zn_2SnO_4, ZnO	SnO_2 , Zn_2SnO_4	SnO_2 , Zn_2SnO_4
9 SZO	40.0	60.0	SnO_2, ZnO	SnO_2 , Zn_2SnO_4, ZnO	Zn_2SnO_4, SnO_2	SnO_2 , Zn_2SnO_4
10 SZO	33.0	67.0	SnO_2, ZnO	ZnO, Zn_2SnO_4, SnO_2	Zn_2SnO_4	Zn_2SnO_4
11 SZO	30.0	70.0	ZnO, SnO_2	ZnO, Zn_2SnO_4, SnO_2	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
12 SZO	20.0	80.0	ZnO, SnO_2	ZnO, Zn_2SnO_4, SnO_2	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
13 SZO	10.0	90.0	ZnO, SnO_2	ZnO, SnO_2	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
14 SZO	5.0	95.0	ZnO, SnO_2	ZnO, SnO_2	Zn_2SnO_4, ZnO	ZnO, Zn_2SnO_4
15 SZO	2.5	97.5	ZnO, SnO_2	ZnO, SnO_2	Zn_2SnO_4, ZnO	ZnO, Zn_2SnO_4
16 SZO	0	100.0	ZnO	ZnO	ZnO	ZnO

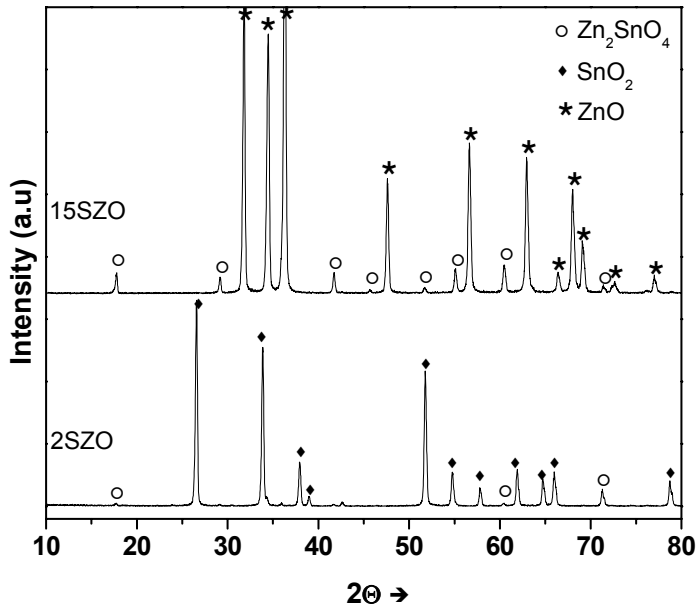

Fig. 3 – XRD patterns of the 2SZO and 15SZO thermally treated at 1300^0C.

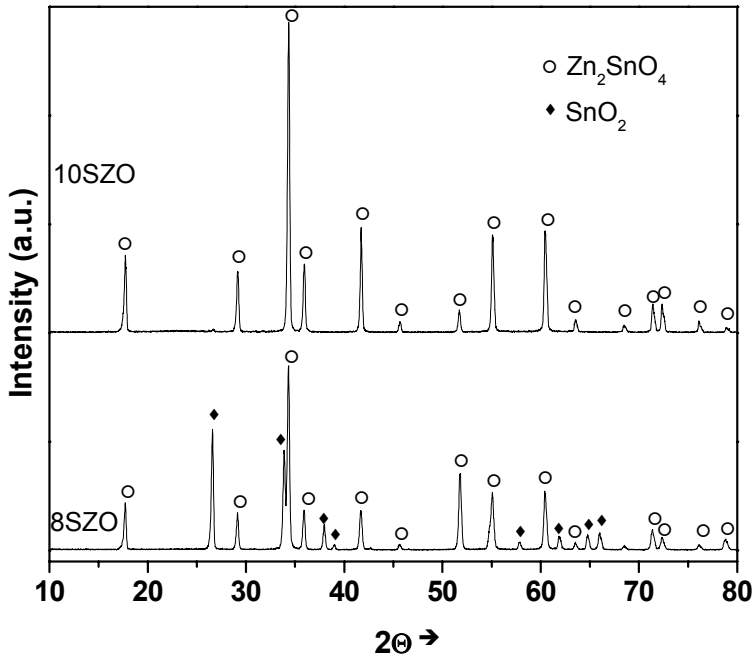

Fig. 4 – XRD patterns of the 8SZO and 10SZO thermally treated at 1300^0C.

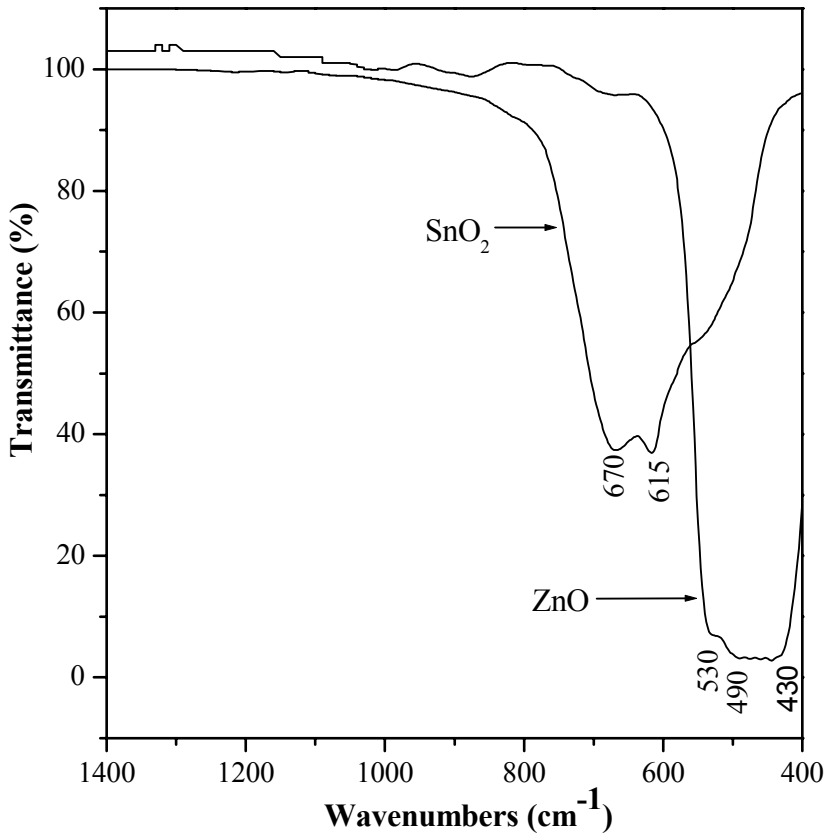

Fig. 5 – FT-IR spectra of the starting oxides.

The results obtained by XRD measurements were confirmed by FT-IR spectroscopy. The FT-IR spectra of the starting oxides (Fig. 5) show typical absorption bands of SnO_2[18] and ZnO[19] lattice.

The FT-IR spectra of the 8SZO sample, as-prepared and thermally treated at different temperatures are presented in Fig. 6. For 8SZO initial mixture the typical absorption bands of SnO_2 lattice at 667 and 616 cm^{-1} and of ZnO lattice at 530, 495 and 440 cm^{-1} were noticed. The 8SZO sample thermally treated at 600°C showed the existence of the same peaks for the SnO_2 lattice but the disappearance of the ZnO typical peaks. Relevant changes in the FT-IR spectrum of the sample thermally treated at 1000°C can be seen by the appearance of new absorption bands at 572 cm^{-1} assigned to the Zn_2SnO_4 spinel phase[20] and a shifting to smaller wave numbers of the vibration bands corresponding to Sn-O (655cm^{-1}) and Zn-O (420 cm^{-1}) bondings. The sample thermally treated over 1000°C exhibits the same FT-IR spectrum but the decrease of the FT-IR bands intensity with increasing of temperature was found.

FT-IR spectra of the 2SZO, 8SZO, 10SZO and 15SZO samples thermally treated at 1300 °C with ten hours plateau are presented in Fig. 7. FT-IR spectrum of the 2SZO sample shows an abnormal transmission decrease and the disappearance of all typical bands belonging to SnO_2 (main phase identified by XRD). A similar behavior was previously observed in the case of SnO_2 based solid solution formation.[21, 22] For the 8SZO and 10SZO samples similar FT-IR vibration bands, but with different intensities, can be observed in good agreement with the XRD data that have shown the presence in these samples of the same spinel phase of zinc stannate.[20] Sample 15SZO keeps the shape and the position of the characteristic bands of ZnO, but the weak and broad absorption band placed at 650 cm^{-1} might also be assigned to the Sn-O bonding.

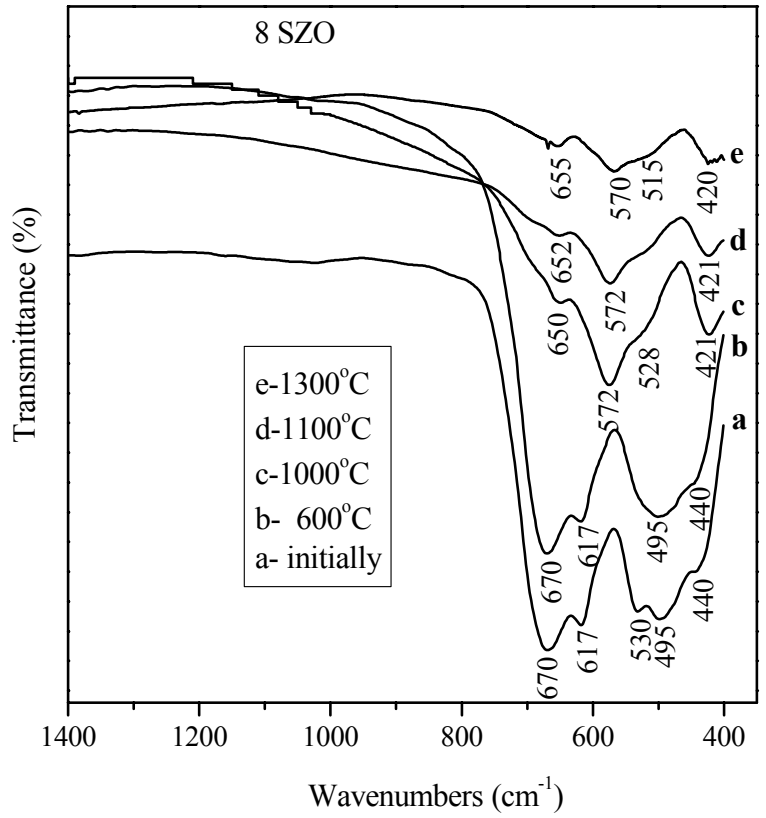

Fig. 6 – FT-IR spectra of the 8SZO sample thermally treated at different temperatures.

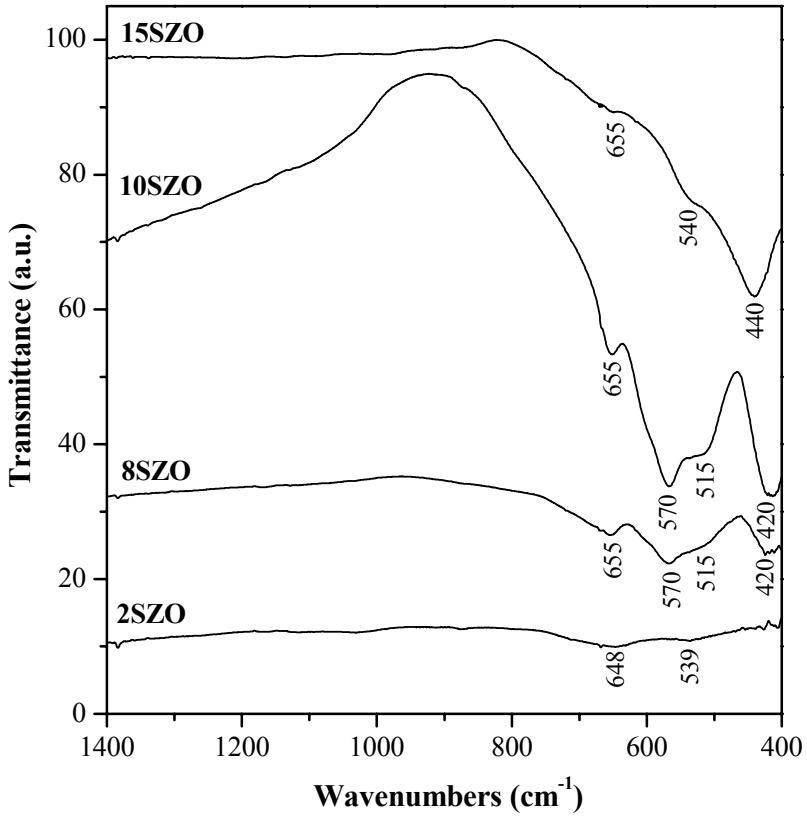

Fig. 7 – FT-IR spectra of selected samples thermally treated at 1300 ^{0}C, 10h.

DISCUSSION

According to the results presented above the solid state reaction between SnO_2 and ZnO over the whole composition range and in the 500-1500 ºC temperature interval leads to the formation of the only Zn_2SnO_4 compound. The reaction of Zn_2SnO_4 formation is the following:

$$SnO_2 + 2ZnO \rightarrow Zn_2SnO_4 \quad (1)$$

This compound was obtained even in non-isothermal condition (with the heating rate of 10ºC/min) up to 1500 ºC although DTA analysis doesn't indicate the presence of any definite thermal effect. It seems that the interaction between the two components takes place continuously. The Zn_2SnO_4 compound was identified by XRD also in the 2SZO sample with 2.5 mol % ZnO, thermally treated starting with 1000ºC.

It is well known that Zn_2SnO_4 has an inverse cubic spinel structure. The unit cell is face-centered cubic (space group $Fd\bar{3}m$ or O_h^7) with lattice parameter a_0 = 8.65 Å.[23] The tetrahedral voids are occupied by Zn^{2+} atoms and the octahedral voids are occupied randomly both by Zn^{2+} and Sn^{4+} atoms.[24, 25] It should be mentioned that Zn^{2+} in tetrahedral coordination has ionic radius of 0.6 Å, but in octahedral coordination its ionic radius is 0.75 Å.[26] The ionic radius of Sn^{4+} is 0.69 Å.[22] It should be mentioned that Sn^{4+} in the SnO_2 rutile type structure adopts octahedral coordination while Zn^{2+} from ZnO wurtzite type structure has a tetrahedral coordination. According to Rečnick *et al*.[26] the formation of octahedral sites in the ZnO lattice is favored by the clustering of Zn- vacancies at the ZnO surface at a temperature higher than 700ºC. The octahedral sites located at the center of the vacancy clusters would be very favorable for Sn^{4+} cations chemisorption and further interaction between the components.

In our experiments formation of the $ZnSnO_3$ compound was not emphasized although Zhang *et al*.[15] reported the obtaining of these compound at 1427 ºC. From a general crystallographic point of view Kovacheva and Petrov[14] however showed that $ZnSnO_3$ cannot adopt a perovskite structure under normal conditions, since the ionic radius of Zn^{2+} is too small. Inaguma *et al.*[17] pointed out that the solid-state reaction between ZnO and SnO_2 in the pressure range from ambient pressure to 5 GPa gives neither $LiNbO_3$(LN)-type $ZnSnO_3$ nor ilmenite (IL)-type $ZnSnO_3$, resulting in a mixture of spinel-type Zn_2SnO_4 and rutile-type SnO_2. The authors also argue that the ilmenite structure is not the thermodynamically favored form at any pressure though the molar volumes of IL-type $ZnSnO_3$ (56.78 $Å^3$) is smaller than that of (1/2 Zn_2SnO_4 + 1/2 SnO_2) (58.3 $Å^3$) and greater than that of LN-type $ZnSnO_3$ (55.97 $Å^3$).

Additional information on the phase formation was given by FT-IR Spectroscopy. Thus for the sample with starting composition of 97.5 mol % SnO_2 and 2.5 mol % ZnO (2SZO) thermally treated at 1300ºC has shown in the FT-IR spectrum an abnormal reduction of transmission and the disappearance of the characteristic bands. Otherwise in XRD patterns characteristics lines corresponding to the Zn_2SnO_4 have a very small intensity in comparison with the sample with starting composition of 97.5 mol % ZnO and 2.5 mol % SnO_2 (15SZO). Nevertheless appearance of FT-IR spectrum similar with those obtained in our previously experiments[21, 22] suggests a partially SnO_2 solid solution formation. The possible equations for substitution of Sn^{4+} with Zn^{2+} are given by Fayat and Castro[27] as following:

$$ZnO \rightarrow Zn''_{Sn} + V_O^{\cdot\cdot} + O_O^x \quad (2)$$

$$V_O^{\cdot\cdot} + e' \rightarrow V_O^{\cdot} \quad (3)$$

$$V_O^x \rightarrow V_O^{\cdot} + e' \quad (4)$$

In this case, zinc ions could adopt octahedral coordination with ionic radius of 0.75 Å.

In Fig. 8 SEM image of the 2SZO is visualized.

Homogeneous surface phase was pointed out by SEM. The presence of SnO_{2ss} solid solution could be assigned to lighter layer surrounding the grains. Further studies are necessary to clarify this aspect.

Based on the results discussed above, the subsolidus phase relations of SnO_2-ZnO system show that the system is divided in two binary subsystems: SnO_2-Zn_2SnO_4 (0-66.6 mol% ZnO initial compositions) and Zn_2SnO_4-ZnO (66.6-100 mol% ZnO initial compositions).

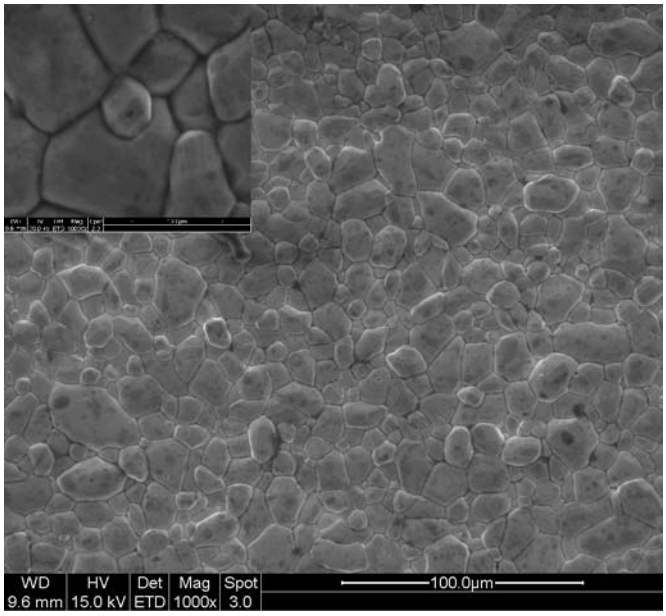

Fig. 8 – SEM image of 2SZO sample thermally treated.

CONCLUSIONS

A systematic study of the phase formation over the whole compositional range of the ZnO-SnO_2 binary system in the 500-1500 ºC temperature domain was approached.

Starting with 900 ºC temperature the formation of the Zn_2SnO_4 with inverse spinel type structure was emphasized in all samples.

The formation of the $ZnSnO_3$ was not observed in the experimental conditions used.

In the 1000-1500 ºC temperature range no change in the phase composition was observed.

The presence of the Zn_2SnO_2 compound divides the system in two subsolidus domains: SnO_2-Zn_2SnO_4 and Zn_2SnO_4-ZnO

FT-IR results confirm the XRD measurements and additionally suggest the limited solid solution formation in the region closed to pure SnO_2.

REFERENCES

1. P.R. Bueno, J. A.Varela and E. Longo, *J. Eur. Ceram. Soc*., **2007**, *27*, 4313.
2. K. Park, J.K. Seong, Y. Kwon, S. Nahm and W.-S.Cho, *Mat. Res.Bull*., **2008,** *43*, 54.
3. S. Major, S. Kumar, M. Bhatnagar and K.L. Chopra, *Appl.Phys.Lett*., **1986**, *49*, 394.
4. Gupta, T. K., *J. Mat. Res.*, **1992**, *12*, 3280.
5. C.H. Kwon, M.N. Hong, D.H. Yun, K. Lee, S.T. Kim, Y.H. Roh and B.H. Lee, *Sens.Actuators*, **1995**, *24-25*, 610.
6. M. Ihoş, F. Manea, G. Bocea and M. Jitaru, *Rev. Roum. Chim.,* **2009**, *54*, 301.
7. A.M. Popescu, G. Nipan, S. Mihaiu, V. Constantin, M. Olteanu and N. Shumilkin, *Rev.Roum.Chim.*, **2010,** *55*, 319.
8. C. Wang, X.M. Wang, B.Q. Xu, J.C. Zhao, B.X. Mai, P.A. Peng, G.Y. Sheng and J.M. Fu, *J. Photochem. Photobiol.A:Chem.,* **2004**, *168*, 47.
9. A. Anastasiou, M.H.J. Lee, C. Leach and R. Freer, *J. Eur.Ceram.Soc*., **2004,** *24*, 1171.
10. T. Hashemi, H.M. Al-allak, J. Illingsworth, A.W. Brinkman and J.Woods, *J. Mater. Sci. Lett.,* **1990,** 7, 776.
11. F. Belliard, P.A. Connor and J.T.S. Irvine, *Solid State Ionics*, **2000,** *135*, 163.
12. N. Nikolic, Z. Marinovic and T. Sreckovic, *J.Mat. Sci.*, **2004**, *39***,** 5239.
13. Y.S. Shen and T. Zhang, *Sens. Actuators B Chem.*, **1993**, *12*, 5.
14. D. Kovacheva and K. Petrov, *Solid State Ionics,* **1998**, *109*, 327.
15. G.Z.Zang, J.F.Wang, H.C.Chen, W.B.Su, W.X.Wang, P.Qi and C.M.Wang, *J. Mat.Sci.,* **2004,** *39*, 3537.
16. H.Q. Chiang, J.F.Wager, R.L. Hoffman, J. Jeong and D.A.Keszler, *Appl. Phys.Lett.*, **2005,** *86*, 013503.
17. Y.Inaguma, M.Yoshida and T.Katsumata, *J. Am. Chem. Soc*., **2008**, *130*, 6704.
18. E.N.Iurchenko and G.N. Kustova, „Kolebantîe spectrî neorganicheskih soedinenii", Ed. Nauk, Novosibirsk, 1981.
19. M. Andrés-Vergés and C.J. Serna, *J. Mater. Sci. Lett*., **1988**, *7*, 970.
20. M. V. Nikolić, T. Ivetić, K. M. Paraskevopoulos, K. T. Zorbas, V. Blagojević and D. Vasiljević-Radović, *J. Eur.Ceram.Soc*., **2007**, *27*, 3727.
21. S. Mihaiu, O. Scarlat, Gh. Aldica and M. Zaharescu, *J. Eur.Ceram.Soc*., **2001**, *21*, 1801.
22. S. Mihaiu, N. Dragan, O. Scarlat, A. Szatvanyi, D. Crisan and M. Zaharescu, *Rev. Roum. Chim.*, **2002**, *47*, 843.
23. D. Segev and S.-H. Wei, *Phys. Rev. B*, **2005**, *71*, 125.
24. W. Su-Huai and S.B. Zhang, *Phys. Rev. B*, **2001**, *63*, 112.
25. R.D. Shannon and C.T. Prewitt, *Acta Cryst.,* **1969**, *B25*, 25.
26. A. Rečnik, N. Daneu and S. Bernik, *J. Eur.Ceram.Soc.,* **2007**, *27*, 1998.
27. J. Fayat and M.S. Castro, *J. Eur.Ceram.Soc*., **2003**, *23*, 1585.