Subsolidus Phase Equilibria in the SnO_2-ZnO binary System

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The present work deals with phase formation studies in the SnO_2-ZnO binary system over the whole concentration range in the 600-1500^{0}C temperature domain.

ABSTRACT

The binary and ternary oxide compounds belonging to the SnO2-ZnO system are very interesting materials for the applications as varistors, electrodes, catalysts and gas and chemical sensors.

The present work deals to investigate the high-temperature interactions of the samples with initial compositions expressed as (1-x) SnO_2-xZnO in order to established the concentration range of the obtaining the phases of interest and thermal stability of them.

XRD, FT-IR Spectroscopy were use to established the formation mechanism of the phases.

Morphological characteristics were investigated by Scanning electron microscopy (SEM) and ceramic properties measurements of apparent porosity, shrinkage and density.

In the 1000-1500 ^{0}C temperature range the initial SnO_2-ZnO binary system turn into SnO_2 – Zn_2SnO_4 and Zn_2SnO_4 –ZnO pseudobinary systems.

Preparation of the samples

Starting materials

- SnO_2 (Merck) - reagent grade
- ZnO (Fluka) - reagent grade

The SnO_2 and ZnO with grain size belong 60 μm and composition presented in Table 1 were wet homogenized in the agate mortar absolute ethanol.

Cylindrical samples with Φ=10 mm and h=2-3 mm were obtained by pressing at 100 MPa.

Thermal treatment:

- Non-isothermal conditions up to 1500^{0}C (heating rate 5^{0}C/minute).
- Isothermal conditions at 600^{0}C - 1500^{0}C; 2 or 10 hours plateau.

Methods of characterization

Structural Characterization:

- XRD analysis was performed with a DRON UM1 diffractometer, 2θ equipped with a graphite monochromatized using Co Kα radiation (λ = 1.79021 Å).
- FT-IR spectroscopy was made with a Nicolet 6700 apparatus in 400-1400 cm^{-1} domain.
- The fluorescence spectra (emission) were recorded with Perkin Elmer 204 spectrofluorimeter (having a Xe lamp of 150 W), interfaced to a computer, permitting a prestabilized reading time of the data. Usually the time range between two measurements is 550 ms.

Morphological characterization:

- Linear shrinkage
- Apparent porosity in methanol
- Arhimedic density
- Scanning electron microscopy

RESULTS

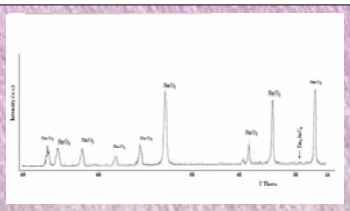
Initial composition of the studied samples

Sample	1SZO	2SZO	3SZO	4SZO	5SZO	6SZO	7SZO	8SZO	9SZO	10SZO	11SZO	12SZO	13SZO	14SZO	15SZO	16SZO
SnO_2 % mol	100	97.5	95	90	80	70	60	50	40	33	30	20	10	5	2.5	-
ZnO % mol	-	2.5	5	10	20	30	40	50	60	67	70	80	90	95	97.5	100

Phase composition of the studied samples

Sample T (^{0}C)	1SZO	2SZO	3SZO	4SZO	5SZO	6SZO	7SZO	8SZO	9SZO	10SZO	11SZO	12SZO	13SZO	14SZO	15SZO	16SZO
600	R*	R, W*	R,W	R, W	R, W	R, W	R, W	R, W	R, W	R, W	R, W	R, W	R, W	R, W	R, W	W
1000	R	R, IS, W*	R, IS, W	R, IS, W	R, IS, W	R, IS, W	R, IS, W	R, IS	R, IS	IS, R, W	IS, W, R	IS, W, R	IS, W, R	IS, W, R	IS, W, R	W
1100	R	R,IS	R, IS	R, IS	R, IS	R, IS	R, IS	R, IS	R, IS	IS	IS, W	IS, W	IS, W	IS, W	IS, W	W
1300	R	R, IS	R, IS	R, IS	R, IS	R, IS	R, IS	R, IS	R, IS	IS	IS, W	IS, W	IS, W	IS, W	IS, W	W

R-Rutile; W- Wurtzhite; IS- Inverse Spinel



XRD pattern of the 2SZO sample

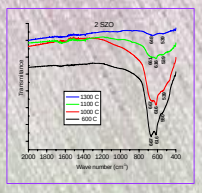
- At 1000 ^{0}C the following reaction take place: $SnO_2 + 2ZnO \rightarrow Zn_2SnO_4$
- The presence of the Zn_2SnO_4 compound even if for 2 SZO sample (2.5% mol ZnO) was observed by X-ray diffraction analysis.
- At temperatures ≥1000^{0}C for the 10SZO sample only Zn_2SnO_4 phase was identified
- At 1300^{0}C following reactions take place

$ZnO \rightarrow Zn_{Sn} + V_{\ddot{o}} + O_{0x}$

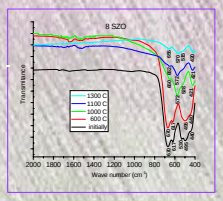
$V_{\ddot{o}} + e' \rightarrow Vo\cdot$

$V_{0x} \rightarrow Vo\cdot + e'$

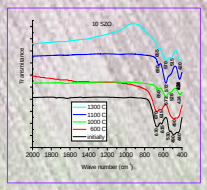
FT-IR Spectroscopy



FT-IR Spectroscopy of the 2SZO sample thermally treated at different temperatures



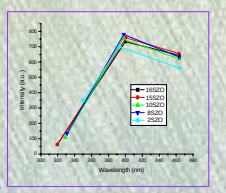
FT-IR Spectroscopy of the 8SZO sample thermally treated at different temperatures



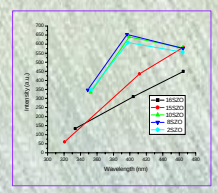
FT-IR Spectroscopy of the 10 SZO sample thermally treated at different temperatures

- For the sample 2SZO at 1300^{0}C IR flattening of IR characteristics bands can be seen. That is due to the SnO_{2ss} solid solutions formation.
- For the sample 8SZO and 10SZO at 1000^{0}C the appearance of the new IR band at 572 cm^{-1} can be observed. This band could be assigned to the Sn-O-Zn bonding in the Zn_2SnO_4 inverse spinel.

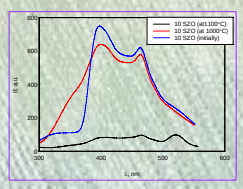
Fluorescence Spectroscopy



The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_f of the initial Sn-Zn oxide mixtures.



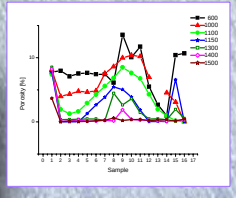
The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_f of the samples thermally treated at 1000^{0}C temperature.



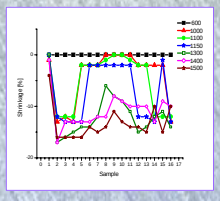
The fluorescence emission spectra of 10 SZO sample thermally treated at different temperatures; λ_{ex} =270 nm

- Initial mixtures of Sn-Zn oxides present similar relative fluorescence intensities.
- In the case of the samples thermally treated at 1000^{0}C smaller relative fluorescence intensities are observed for the samples 15SZO and 16SZO (with highest ZnO content).
- For the samples thermally treated at 1100^{0}C the fluorescence emission quenched due to the formation of the Zn_2SnO_4 compound probably.

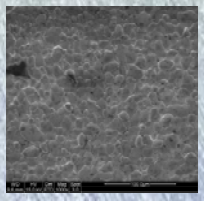
Morphological characterization



Apparent porosity of the samples



Linear shrinkage of the samples



SEM image of the 2SZO sample

CONCLUSIONS

- Phase formation in the SnO_2-ZnO binary system in the whole concentration range in the 600-1500^{0}C temperature domain was studied.
- At 1000 ^{0}C the Zn_2SnO_4 compound with inverse spinel structure was formed. The coordination change of the Zn ions due to the formation of the inverse spinel was emphasized by FT-IR.
- Solid solutions with rutile structure were formed at 1300 ^{0}C in the riche SnO_2 domain.
- Dense ceramics with relative density, higher then 95%, were obtained in both riche SnO_2 and ZnO domains.
- All the mechanical mixtures belonging to the SnO_2-ZnO system excepting pure SnO_2 present fluorescence emission in UV range as well as the ceramics obtained after thermal treatment at 1000 ^{0}C. The coordination change of Zn ions through formation of Zn_2SnO_4 inverse spinel quenched fluorescence emission.

Acknowledgments

The financial support of the Romanian National Management Program, PN II type Project under the contract no. D11 048/18.09-2007 is gratefully acknowledged.