Phase Formation 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 concentration range in the 600-1500^{0}C temperature domain.

ABSTRACT

The Sn-Zn-O ceramics are very interesting materials for the 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 1000-1500^{0}C domain were evaluated by XRD and FT-IR Spectroscopy.
Morphological characteristics were determined from linear shrinkage, porosity and density measurements and Scanning electron microscopy (SEM).
Besides SnO_2 and ZnO only Zn_2SnO_4 ternary compound was found in our experimental conditions.
A correlation of the observed fluorescence emission in the Sn-Zn-O samples with structural changes resulting from interactions during the thermal treatments was established.

EXPERIMENTAL

Preparation of the samples

Starting materials

- **SnO_2** (Merck) - p.a reagent grade
- **ZnO** (Fluka) - p.a 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

Structural characterization

XRD

Table 1 Initial and phase composition of the studied samples

Sample	Initial Composition (mol %)		Phase composition			
	SnO_2	ZnO	600 ^{0}C	1000 ^{0}C	1100 ^{0}C	1300 ^{0}C
1SZO	100	-	SnO_2	SnO_2	SnO_2	SnO_2
2SZO	97.5	2.5	SnO_2,ZnO	SnO_2, Zn_2SnO_4, ZnO	SnO_2,Zn_2SnO_4	SnO_2(ss)
3SZO	95	5	SnO_2,ZnO	SnO_2, Zn_2SnO_4,ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
4SZO	90	10	SnO_2,ZnO	SnO_2, Zn_2SnO_4, ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
5SZO	80	20	SnO_2,ZnO	SnO_2, Zn_2SnO_4,ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
6SZO	70	30	SnO_2,ZnO	SnO_2, Zn_2SnO_4, ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
7SZO	60	40	SnO_2,ZnO	SnO_2, Zn_2SnO_4,ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
8SZO	50	50	SnO_2,ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
9SZO	40	60	SnO_2,ZnO	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4	SnO_2,Zn_2SnO_4
10SZO	33	67	SnO_2,ZnO	Zn_2SnO_4, SnO_2, ZnO	Zn_2SnO_4	Zn_2SnO_4
11SZO	30	70	SnO_2,ZnO	Zn_2SnO_4, ZnO, SnO_2,	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
12SZO	20	80	SnO_2,ZnO	Zn_2SnO_4, ZnO, SnO_2,	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
13SZO	10	90	SnO_2,ZnO	Zn_2SnO_4, ZnO,SnO_2,	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
14SZO	5	95	SnO_2,ZnO	Zn_2SnO_4, ZnO, SnO_2,	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
15SZO	2.5	97.5	SnO_2,ZnO	Zn_2SnO_4, ZnO, SnO_2,	Zn_2SnO_4, ZnO	Zn_2SnO_4, ZnO
16SZO	-	100	ZnO	ZnO	ZnO	ZnO

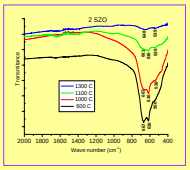
ASTM Files:
SnO_2: 5-467;
ZnO: 5-664;
Zn_2SnO_4: 24-147

At 1000 ^{0}C the following reaction take place:

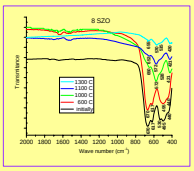
$$SnO_2 + 2ZnO \rightarrow Zn_2SnO_4$$

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.

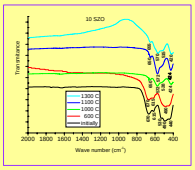
FT-IR Spectroscopy



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



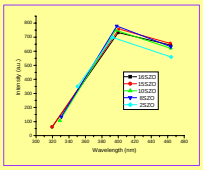
FT-IR Spectroscopy of the 8SZO sample thermally treated at different temperatures



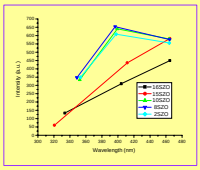
FT-IR Spectroscopy of the 10 SZO sample thermally treated at different temperatures

For the sample 2SZO at 1300^{0}C IR flattening of IR characteristics bands can be seen. That is due to the solid solutions formation of $SnO_{2\text{-}ss}$.
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 of the Zn_2SnO_4 inverse spinel.

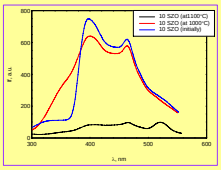
Fluorescence Spectroscopy



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



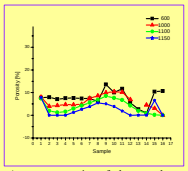
The fluorescence emission maxima, λ_{em}, and relative fluorescence intensities, I_f of the samples thermally treated at 1000^{0}C temperature.



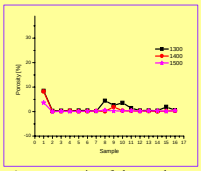
The fluorescence emission spectra of 10 SZO sample thermally treated at different temperatures; λex =270 nm

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 samples15SZO 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.

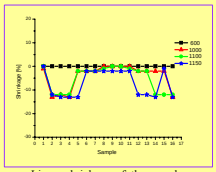
Morphological characterization



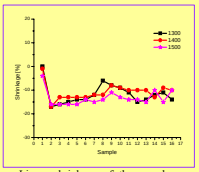
Apparent porosity of the samples thermally treated at different temperatures, 10 h plateau.



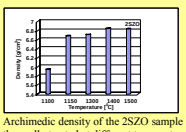
Apparent porosity of the samples thermally treated at different temperatures, 90 min. plateau.



Linear shrinkage of the samples thermally treated at different temperatures, 10 h plateau



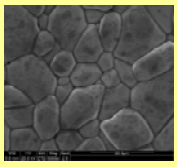
Linear shrinkage of the samples thermally treated at different temperatures, 90 min. plateau



Archimedic density of the 2SZO sample thermally treated at different temperature

Table 2 Relative Density of the selected samples thermally treated at 1500^0 C, 90 min.

Sample	Relative Density (%)
1SZO	69.40
2SZO	98.27
15SZO	95.07
16SZO	96.05



SEM image of the 2SZO sample

At 1500^{0}C 2SZO sample presents the highest relative density, for which no secondary phase was visualized by SEM.
Probably the densification occurs by the formation of oxygen vacancies according to the following reaction:

$$ZnO \rightarrow Zn_{Sn}^{\cdot} + V_{\ddot{o}} + O_0^x$$
$$V_{\ddot{o}} + e^{\cdot} \rightarrow V_{\ddot{o}}^{\cdot}$$
$$V_{\ddot{o}}^{x} \rightarrow V\ddot{o} \cdot + e^{\cdot}$$

CONCLUSIONS

- Phase formation in the SnO_2-ZnO binary system in the whole concentration range on 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 change coordination of the Zn ions due to the formation of the inverse spinel was emphasized by FT-IR.
- Solid solutions with rutile structure was 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 change coordination of Zn ions through formation of Zn_2SnO_4 inverse spinel quenched fluorescence emission.

Acknowledgments

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