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A DETAILED XRD AND FTIR ANALYSIS OF Bi_2O_3 DOPED ZnO SnO_2 CERAMICS

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ABSTRACT

ZnO-SnO_2 ceramics were prepared with a traditional powder mixed oxide route by mixing starting powders of ZnO and SnO_2 in the molar ratio 2:1 and adding small amounts (0.5; 1.0 and 1.5 molar%) of Bi_2O_3. These mixtures were then mechanically activated for 10 minutes in a planetary ball mill, uniaxially pressed and sintered at 1300ºC for 2h. The phase composition of the sintered samples was determined with X-ray Diffraction (XRD) analysis and a detailed Rietveld analysis was performed. Room temperature far infrared reflectivity diagrams were obtained using Bruker 113V FTIR spectrometer and fitted with several theoretical models in other to determine parameter values for some structural and optical properties of the obtained material.

INTRODUCTION

The ZnO-SnO_2 system has been the subject of intensive research, mostly in the field of varistor ceramics. Spinel type ZnO-SnO_2 ceramics are obtained by solid-state reaction sintering already at 900°C starting from a compacted powder mixture of ZnO and SnO_2 in the molar ratio 2:1. The newly formed compound, zinc stannate, with a general formula Zn_2SnO_4, belongs to the cubic oxide spinel group of compounds. Zinc stannate has potential application as a material for gas and humidity sensing, anodes for Li-ion batteries and as semiconducting working electrodes for solar cells. Cubic spinel zinc stannate in bulk form is stable in the inverse spinel structure, with a face-centered cubic (fcc) unit cell (Fd3m space group, origin 3m), so Zn^{2+} occupy 8a sites and both Zn^{2+} and Sn^{4+} cations occupy 16d sites, while O occupies 32e sites. Spinel type structures can have big cation disorders in the crystal lattice and certain nonstoichiometry. Nevertheless, disorders in spinel structures are non conventional so there is no change in symmetry. Addition of small amounts of Bi_2O_3 to the ZnO-SnO_2 system creates conditions for liquid phase sintering and enhances the densification process. Addition of Bi_2O_3 to the 2ZnO-SnO_2 system resulted in the formation of a Zn_2SnO_4-SnO_2 two-phased system, with larger regions of pure Zn_2SnO_4 and smaller areas of residual SnO_2.

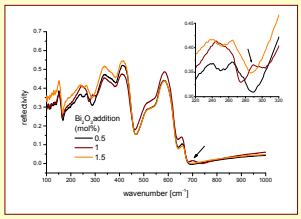


Figure 2. Measured infrared reflectivity spectra of sintered samples.

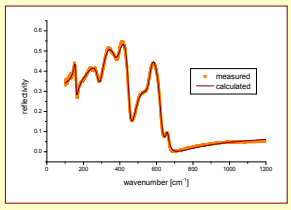


Figure 3. Measured (dotted line) and calculated (full line)-with model of coupled oscillators, infrared reflectivity spectra of sintered sample with 1.5 mol% Bi_2O_3.

RESULTS

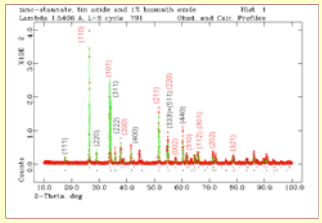
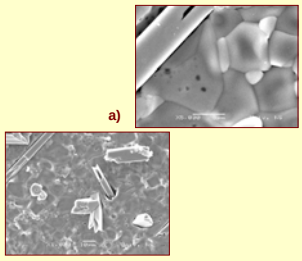
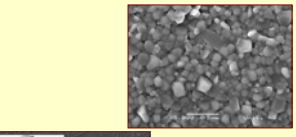
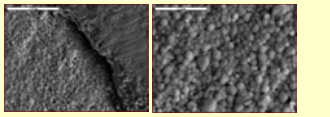
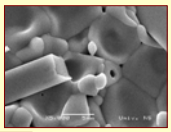


Figure 1. Rietveld refinement of XRD diagram obtained for sample with 1.0 mol% of Bi_2O_3.









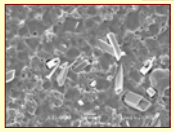


Figure 6. SEM images of sintered samples with a) 0.5, b) 1.0 and c) 1.5 mol% of Bi_2O_3.

Table 1. Weight fractions of Zn_2SnO_4 and SnO_2 in samples obtained by Rietveld refinement.

Sample	ZSO-0.5	ZSO-1	ZSO-1.5
Zn_2SnO_4	0.58714	0.46038	0.99268
SnO_2	0.41286	0.53962	0.00732

Table 2. Lattice parameters of SnO_2 in samples.

Sample		ZSO-0.5	ZSO-1	ZSO-1.5
Cell parameter	*a=b*	4.72829	4.73804	4.72538
	c	3.19295	3.18586	3.18234

Table 3. Structure parameters of Zn_2SnO_4 in samples.

Sample		ZSO-0.5	ZSO-1	ZSO-1.5
Cell parameter	*a*	8.65773	8.66067	8.65641
O	*u*	0.2572	0.2538	0.2573
Zn fraction	T	0.8614	0.9088	0.8229
	M	0.5693	0.5456	0.5886
Sn fraction	T	0.1383	0.0912	0.1771
	M	0.4307	0.4544	0.4114
Bond lengths	T-O	1.98248	1.93287	1.98362
	M-O	2.10391	2.13233	2.10281
Inversion degree	*x*	0.8614	0.9088	0.8229
Temperature factors	U_T	0.01973	0.00767	0.02066
	U_M	0.00399	0.01334	0.00139
	U_O	0.01455	0.01351	0.04231

CONCLUSIONS

- Two phased system composed of Zn_2SnO_4 and SnO_2 phases was formed and structure parameters of these two phases were determined by Rietveld analysis (the amount of SnO_2 varied depending on the amount of added Bi_2O_3 between 0.7 and 54%).
- No peaks of Bi_2O_3 or its secondary peak phases were observed.
- Addition of Bi_2O_3 caused increase of relative density up to 92% for sample with addition of 1.0 mol% of Bi_2O_3.
- Far infrared reflectivity spectra were analyzed in view of changes in the sample composition and peaks originating from SnO_2 were only noted in the sample containing 54% SnO_2.
- The model of coupled oscillators is really only applicable to single-phase samples, so in the case of sample with 1.5 mol% Bi_2O_3, where influence of SnO_2 is negligible (0.7%), eight determined oscillators originate from Zn_2SnO_4, while in the case of other two samples, especially sample with 1.0 mol% of Bi_2O_3 determined oscillators originate from mixture of Zn_2SnO_4 and SnO_2 and determined parameter values are just illustrative.
- The extra modes for Zn_2SnO_4, compared to four predicted by group theory for normal spinel structures, possibly originated from cation disorder in the crystal lattice.

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