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A DETAILED XRD AND FTIR ANALYSIS OF Bi₂O₃ DOPED ZnO-SnO₂ CERAMICS

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ABSTRACT

ZnO-SnO₂ ceramics were prepared with a traditional powder mixed oxide route by mixing starting powders of ZnO and SnO₂ in the molar ratio 2:1 and adding small amounts (0.5; 1.0; and 1.5 molar%) of Bi₂O₃. These mixtures were then mechanically activated for 10 minutes in a planetary ball mill, uniaxially pressed and sintered at 1300°C 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 order to determine parameter values for some structural and optical properties of the obtained material.

INTRODUCTION

Spinel type ZnO-SnO₂ ceramics are obtained by solid-state reaction sintering already at 900°C [1] starting from a compacted powder mixture of ZnO and SnO₂ in the molar ratio 2:1. The newly formed compound, zinc stannate, belongs to the cubic oxide spinel group of compounds with a general formula Zn₂SnO₄. Zinc stannate has potential application as a material for gas and humidity sensing [2, 3], anodes for Li-ion batteries [4] and as semiconducting working electrodes for solar cells [5, 6]. Cubic spinel zinc stannate in bulk form is stable in the inverse spinel structure [7], with a face-centered cubic (fcc) unit cell (Fd $\bar{3}$ m space group, origin $\bar{3}$ m), so Zn²⁺ occupy 8a sites and both Zn²⁺ and Sn⁴⁺ cations occupy 16d sites, while O occupies 32e sites. Spinel type structures can have big cation disorders in the crystal lattice and certain nonstoichiometry [8]. Nevertheless, disorders in spinel structures are non conventional so there is no change in symmetry. Addition of small amounts of Bi₂O₃ to the ZnO-SnO₂ system creates conditions for liquid phase sintering and should enhance the densification process [9]. Addition of Bi₂O₃ to the 2ZnO-SnO₂ system resulted in the formation of a Zn₂SnO₄-SnO₂ two-phased system, with larger regions of pure Zn₂SnO₄ and smaller areas of residual SnO₂ [10, 11].



EXPERIMENTAL

Commercially available zinc oxide (ZnO, Aldrich) and tin oxide (SnO₂, Aldrich) powders were mixed in the 2:1 ratio. After adding 0.5; 1.0 and 1.5 molar% of bismuth oxide (Bi₂O₃) this mixture was homogenized in absolute ethanol dried at 70°C and mechanically activated in a planetary ball mill (Fritsch Pulversette 5) for 10 min. These powder mixtures were then uniaxially pressed under 980MPa and sintered (Lenton Thermal Designs Type 1600) at 1300°C for 2h. Appropriate samples were denoted as ZSO-0.5, ZSO-1 and ZSO-1.5, for samples with addition of 0.5; 1.0 and 1.5 molar% of Bi₂O₃, respectively. X-ray analysis of the obtained samples was conducted on an X-ray diffractometer (Philips PW-1710) with λ Cu K α radiation and a step scan mode of 0.02°/2s in the range 10-100° (2 θ). Structural refinement was carried out by Rietveld method using a GSAS package [12]. Initial cell parameters for Zn₂SnO₄ were taken from ICSD 28235 (Choisnet et al. [13]), where the cell parameter $a=8.65$, anion displacement parameter $u=0.39$ (0.265 for origin $\bar{3}m$). No temperature parameters were available so we started from the default program values. The degree of inversion (x) was allowed to vary, thus Zn²⁺ and Sn⁴⁺ cations can be on 8a and 16d sites. All sites were assumed to be fully occupied. SnO₂ was refined in space group P4₂/mnm. Initial cell parameters, $a=b=4.735$, $c=3.1837$, temperature parameters and the anion displacement parameter (0.3096) were taken from ICSD 90611 (Klementova et al. [14]). The microstructure of the sintered samples was examined with SEM-JEOL JSM 646OLV. Room temperature far infrared reflectivity measurements were performed with near normal incident light in the range between 100 and 1000 cm⁻¹ using a Bruker 113V FTIR spectrometer.

RESULTS AND DISCUSSION

XRD patterns of analyzed samples were shown in ref. [11]. Rietveld analysis of XRD patterns, for Bi₂O₃ doped ZnO-SnO₂ ceramics, confirmed formation of a two phased system composed of Zn₂SnO₄ and SnO₂ phases, as calculated weight fractions (w_p , %) gave values from ~59% Zn₂SnO₄ and 41% SnO₂ in ZSO-0.5 to 99% Zn₂SnO₄ and ~1% SnO₂ in ZSO-1.5 [15].

Example of analyzed XRD diagrams with Rietveld method is given in Fig. 1 for sample ZSO-1.5. A small peak of Al at about 44.6° (2 θ) was noted in all samples. It originates from the sample frame/base, which was used during diffraction measurements. No peaks of Bi₂O₃ or its secondary peak phases were observed in the analyzed diffractograms, due to too small amounts of added Bi₂O₃, which were under the detection limit of the XRD technique, or Bi₂O₃ evaporation during the sintering process at such a high temperature (1300°C) [11].

Addition of Bi₂O₃ to the ZnO-SnO₂ system caused increase of relative density up to ~92% for investigated mixtures, as expected, compared to the non-doped samples where the relative density was ~84% [11]. Samples ZSO-0.5 and ZSO-1.5 have a similar microstructure composed of Zn₂SnO₄ and pinned SnO₂ particles (Fig. 2). The most dense sample with most homogenous microstructure was the sample with the addition of 1.0 molar% of Bi₂O₃ (ZSO-1).

So, the optimal amount of Bi₂O₃ for the enhancement of the densification process and formation of the most dense ZnO-SnO₂ ceramics, in the sintering temperature-time regime of 1300°C-2h is 1.0 molar%. Fig. 3 shows a SEM image of the ZSO-1 sample.



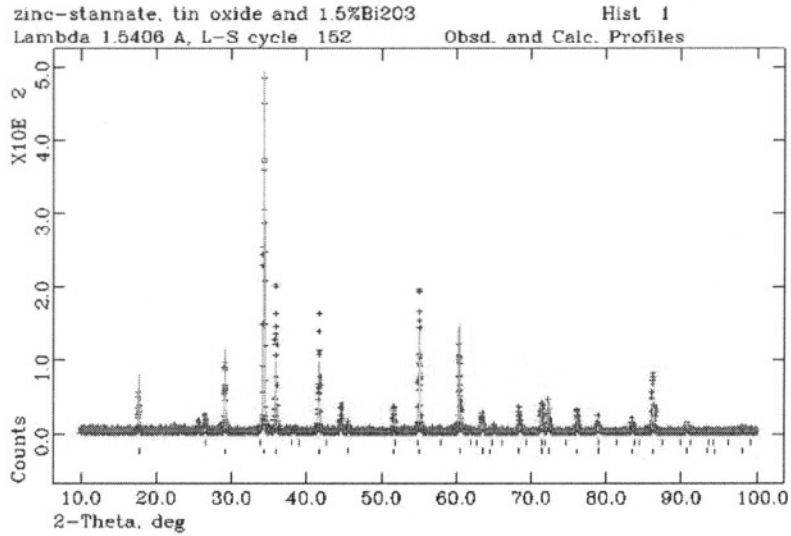


Fig. 1 Rietveld refinement of XRD diagram obtained for sample ZSO-1.5

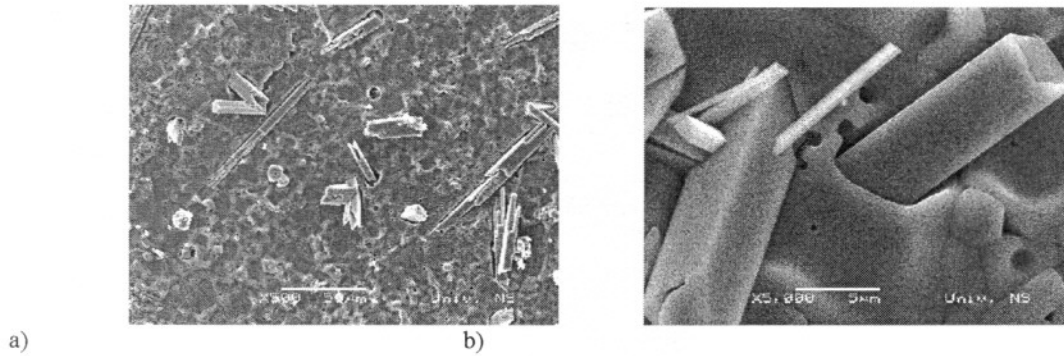


Fig. 2 SEM images of a) ZSO-0.5 and b) ZSO-1.5 samples

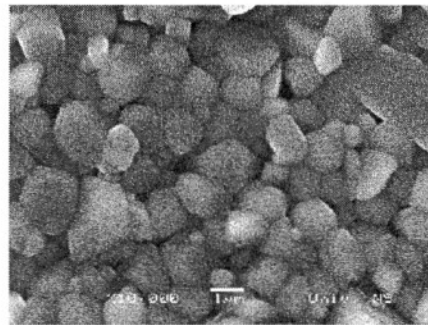


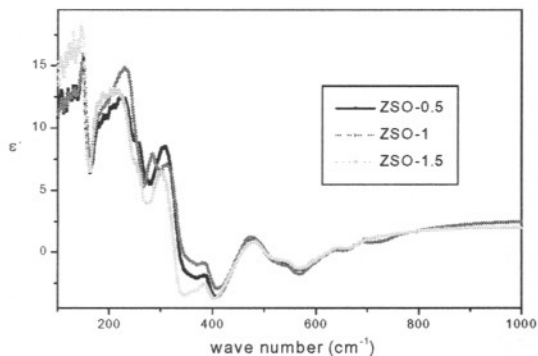
Fig. 3 SEM image of ZSO-1 sample

Structural parameters obtained for Zn_2SnO_4 in analyzed samples, are given in [15] and showed that the lattice parameter values (a) are similar for all samples (8.65 Å for ZSO-05 and ZSO-15 and 8.66 Å for ZSO-1), the inversion degree is between 82% and 94% thus Zn_2SnO_4 is

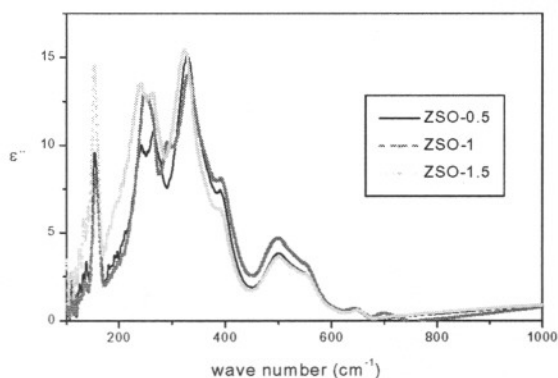


in the inverse spinel structure, as expected, but there is some disorder in the structure. The anion displacement parameter (u) values were similar (0.257) and lowest for ZSO-1 (0.254). All were slightly lower than the value obtained by Choiznet et al. (0.265) [13] and more similar to the theoretically calculated value of 0.2583 [16]. In all cases the anion displacement parameter value (u) was higher than its ideal value, resulting in increased tetrahedral bond lengths and decreased octahedral bond lengths compared to ideal values [17].

The measured reflectivity diagrams for all analyzed samples as a function of the wave number were given elsewhere [10, 15]. The reflection diagrams were first analyzed using the Kramers-Kronig (K-K) method. Determination of the refractive index, n , and extinction coefficient, k , enabled calculation of the change of the complex dielectric permittivity and dielectric loss function. The peaks of the imaginary part of the complex dielectric function (ϵ'') practically correspond to positions of transversal optical modes, while maximums of the dielectric loss function are at positions of longitudinal modes. Fig. 4 shows wave number dependence of the real, a) and imaginary, b) part of the complex dielectric function, calculated with (K-K) method using measured reflectivity diagrams.



a)



b)

Fig. 4 Change of the real, a) and imaginary, b) part of the complex dielectric permittivity function versus wave number for ZSO-0.5, ZSO-1 and ZSO-1.5 samples



The four-parameter model first introduced by Gervais and Piriou [18] was then used to analyze the measured diagrams. Eight oscillators were determined for samples ZSO-0.5 and ZSO-1.5. A ninth one was determined for sample ZSO-1. The obtained parameter values, transverse and longitudinal frequencies, transversal and longitudinal damping factors and high frequency dielectric permittivity contribution are shown elsewhere [15]. Previous investigations on this topic proved that the extra peak for ZSO-1 originated from the highest and the most intensive E_u bulk mode of SnO_2 [10], that shifted to a higher frequency, as noted previously in literature [19-21]. The model of coupled oscillators is really only applicable to single-phase samples. The determined oscillators for the sample ZSO-1.5 originate from Zn_2SnO_4 because it contains a small amount of SnO_2 , which makes the influence of SnO_2 negligible. In the case of ZSO-0.5 and ZSO-1 the determined oscillators originate from the mixture of Zn_2SnO_4 and SnO_2 and stand only as illustrative values.

Group theory predicts four infrared modes for normal $\text{Fd}\bar{3}m$ spinel structures [15]. We determined eight for samples ZSO-0.5 and ZSO-1.5. This is in accordance with our previous analysis of bulk Zn_2SnO_4 [22] where we determined eight oscillators compared to seven determined for thin film Zn_2SnO_4 [23, 24]. The dominant Zn_2SnO_4 phase in ZSO-1.5 has an inverse spinel structure, even though the cation inversion is not 1 (0.83), as there is some cation disorder in the crystal lattice. EDS analysis [10, 11] performed on these samples showed that the composition of Zn_2SnO_4 is with some non-stoichiometry.

This work is part of intensive and continuing research [10, 11, 15] for better insight on the effects of small Bi_2O_3 addition to the formation of spinel type ZnO-SnO_2 ceramics and its structural, optical and electrical properties.

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