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SUBSTITUTION OF COUPLE Sn(IV)/Zn(II) FOR In(III) IN THE FLUORITE-LIKE TRANSPARENT CONDUCTORS: $In_{5-2X}Sn_{1+X}SbZn_XO_{12}$

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ABSTRACT. Three new compositions (x = 0.1, x = 0.2 and x = 0.3) belonging to $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system, have been successfully synthesized by substitution of pair Sn(IV)/Zn(II) for In(III). The compositions were studied from point of view of structural, optical and electrical properties. Structure calculations shows an ordered cationic distribution over the octahedral and highly distorted sevenfold coordinated site. For $In_{4.4}Sn_{1.3}SbZn_{0.3}O_{12}$ composition a small amount of unreacted SnO_2 was identified, which decreases from 5.76 wt % to 3.17 wt %, by increasing preparation temperature from 1300 °C to 1350 °C. The electrical conductivity of the x = 0.1 composition was enhanced by approximately one order of magnitude with respect to $In_4Sn_3O_{12}$.

Keywords: *indium-based transparent conductors, oxygen-deficient fuorite-type structure, optical properties, electrical properties.*

INTRODUCTION

Due to the fact that a critical component in all flat panel displays (FPDs) are the electrodes which control the orientation of the liquid-crystal molecules, many effort are focuses on the discovery of new n- or p- type transparent conducting oxides (TCOs) [1]. TCOs oxide compositions space is dominated by following oxides and their combination: ZnO, In_2O_3, Ga_2O_3, SnO_2 and CdO. Besides the most famous ITO (In_2O_3:Sn), which combine highest transmissivity for visible light with the lowest electrical resistivity, another indium-rich oxide, with properties

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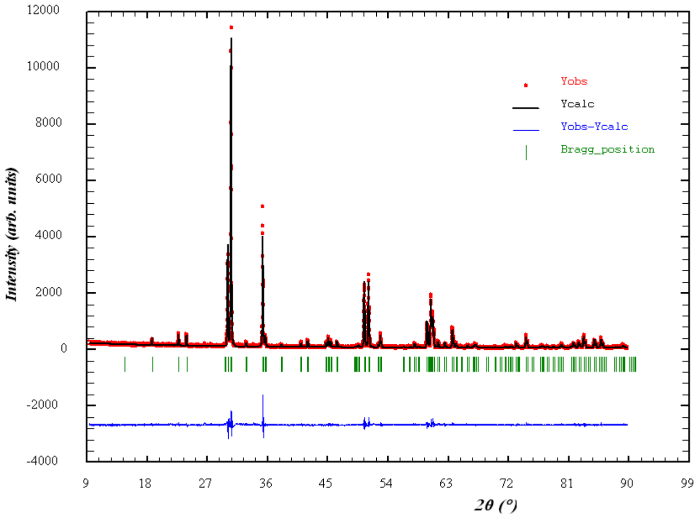
close to ITO, was identified for the composition $In_4Sn_3O_{12}$. The structural studies of the later showed a rhombohedral unit cell which is viewed in a hexagonal basis, and is in fact a doubly ordered oxygen-deficient fluorite structure. Within the unit cell, there are two nonequivalent cationic sites, the six coordinate 3*a* position, a distorted cube with anion vacancies on a pair of opposite vertices, and a general 18*f* position, sevenfold coordinated with anions sets at the corners of a highly distorted cube with a vacancy at one vertex [2]. As previously shown, the 3*a* positions are exclusively occupied by the Sn cations, while the 18*f* positions are occupied by both Sn and In cations. Several transparent conductors have been previously reported [3-5], which shown that introduction of antimony revealed a great abillity to form M_7O_{12} ordered oxygen-deficient fluorite structure [6]. Moreover, by the synthesis of $In_{4+x}Sn_{3-2x}Sb_xO_{12}$ solid solution, the electrical properties of In_5SnSbO_{12} composition were improved by increasing the electronic conductivity up to one order of magnitude if compare to $In_4Sn_3O_{12.}$ First-principles band-structure calculations performed on these compositions demonstrate strong similarities between the electronic structures of $In_4Sn_3O_{12}$ and In_5SnSbO_{12} which suggest comparable physical properties in these materials [7, 8]. Consequently, the aim of this work is to investigate the possible substitution of the pair Sn(IV)/Zn(II) for In(III) in M_7O_{12} structure. $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system was analysed from point of view of structural, optical and electrical properties.

EXPERIMENTAL

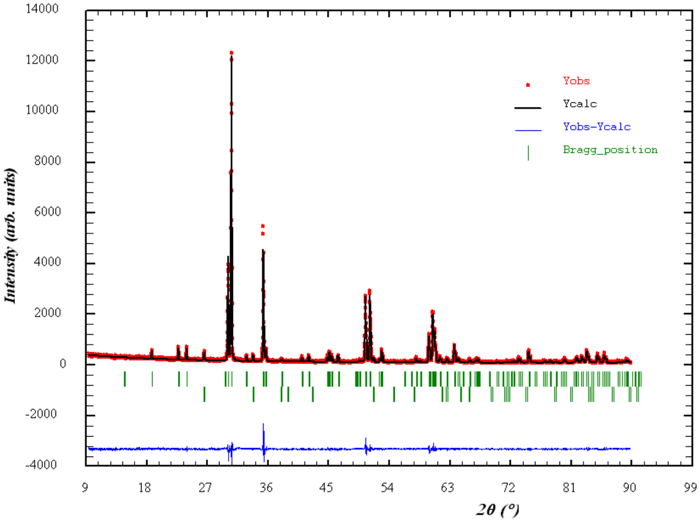
Different compositions with the M_7O_{12} structure were prepared from mixtures of pure In_2O_3, SnO_2, Sb_2O_3 and ZnO, in alumina crucibles heated in air up to 1300 °C and 1350 °C, respectively. Crystalline phases were determined by X-ray diffractometry (XRD, Shimadzu 6000) using Cu-Kα radiation ($\lambda = 1.5406$ Å) equipped with Ni-filter in a 2θ range of 5°-90°. The patterns were analyzed using Rietveld method (FullProf program [9]). The diffuse reflectance spectra of the as-prepared compositions were recorded with a double beam spectrophotometer (Cary Varian 100 Spectrofotometer) in the range 190-900 nm with a scan rate of 600 nm/min. The electrical resistivity of pellets sintered in air at 1350 °C was measured at room temperature by the four-probe method using a PPMS facility.

RESULTS AND DISCUSSION

XRPD structure calculation were performed in terms of a Rietveld analysis of the diffractograms, using the structural model of $In_4Sn_3O_{12}$, S.G. $R\bar{3}$, with two sets of cationic positions 3(a), 18(f) and three sets of oxygen positions 18(f), in the corresponding hexagonal cell. Results obtained from the Rietveld analysis of three compositions of the $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system, corresponding to two different temperature, 1300 °C and 1350 °C, are reported in Table 1. For the different compositions analyzed, the convergence of the refinements was easily obtained, resulting in satisfying values of the reliabilty factors. For comparison, the data concerning $In_4Sn_3O_{12}$ ($x = 0$) and our previous results obtained from XRPD Rietveld analysis for In_5SnSbO_{12} [6] are also reported. The calculated patterns fit with the experimental one, as exemplified for the $x = 0.1$ and $x = 0.3$ compositions (Fig.1). For $In_{4.4}Sn_{1.3}SbZn_{0.3}O_{12}$ composition a small amount of unreacted SnO_2 was identified. Consequently, for $x = 0.3$ composition it was decided to systematically include in the calculation procedure the possible extra phases SnO_2. One can notice the presence of corresponding supplementary bars in Fig. 1b. In the retained example the calculated amount of the extra phases is equal to 5.76 wt% and 3.17 wt%, respectively. It should be emphasized that increasing temperature from 1300 °C to 1350 °C a decrease of secondary phase amount, was evidenced. Regarding the cationic distribution the 3(a) sites are preferentially occupied by antimony, whereas the additional Sb is statistically distributed in the 18(f) sites together with In and Zn. This cationic distribution is also supported by the tendency of Sb^{5+} to accomodate a highly symmetrical octahedral coordination, as previously demonstrated [10]. The smaller size of Sb^{5+} compared to In^{3+}, Sn^{4+} and Zn^{2+}, according to Shannon and Prewitt [11], are in agreement with this view point.



a)



b)

Fig. 1. Observed (dots), calculated (lines) and difference XRPD pattern of x = 0.1 (a) and x = 0.3 (b) composition, after heating at 1350 °C.

Table 1. Crystal chemical data for the compositions x = 0.1, x = 0.2 and x = 0.3 of the $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system and compare to In_5SnSbO_{12}[6].

Comp. x	Temperature (°C)	Cell parameters			Reliability factors		
		a (Å)	c (Å)	V (Å)^3	Rb	Rp	χ^2
x = 0 [6]	1400 °C	9.4478(2)	8.9034(2)	688.76	4.7	12.5	-
x = 0.1	1300 °C	9.443854	8.903104	687.655	4.21	11.9	2.725
	1350 °C	9.453803	8.911015	689.717	4.52	13.9	2.238
x = 0.2	1300 °C	9.44517	8.906440	688.184	3.96	12.5	2.828
	1350 °C	9.445716	8.907287	688.534	3.56	12.8	2.296
x = 0.3	1300 °C	9.439899	8.901480	686.954	3.38	12.1	2.129
	1350 °C	9.444859	8.904285	687.893	3.37	13.5	2.034

Figure 2 shows the diffuse reflectance (%R) spectra of x = 0.1, x = 0.2 and x = 0.3 compositions belonging to $In_{5-2}xSn_{1+x}SbZn_xO_{12}$ system, prepared at 1350 °C. All samples exhibit a reflectance varied from 7-5% at wavelengths approximately 450 nm. The reflectance spectra of $In_{4.4}Sn_{1.3}SbZn_{0.3}O_{12}$, and $In_4Sn_3O_{12}$ and In_5SnSbO_{12} for comparison, are displyed in Fig. 3. One indeed observes that introduction of tin and zinc in the presence of antimony, decreases the maximum percent reflectance around 450 nm, by approximately 10%, with respect to $In_4Sn_3O_{12}$ and In_5SnSbO_{12}, respectively. Simultaneously, a small shift of the optical bandgap to higher energies, occurs.

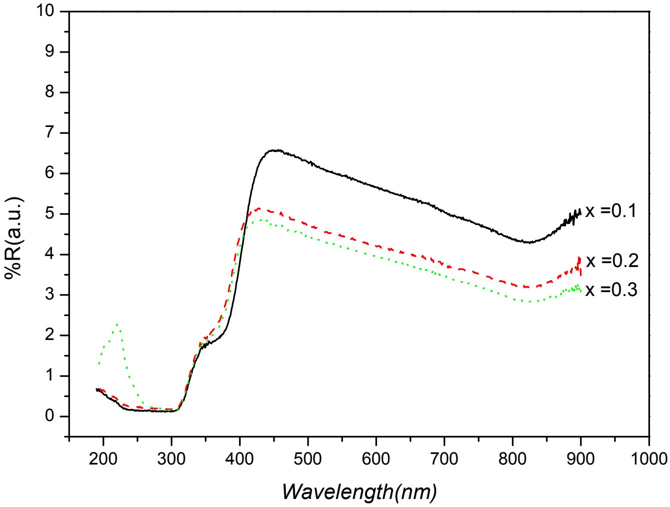


Fig. 2. Measured optical reflectance spectra in the compositions x = 0.1, x = 0.2 and x = 0.3 of the $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system, after heating at 1350 °C.

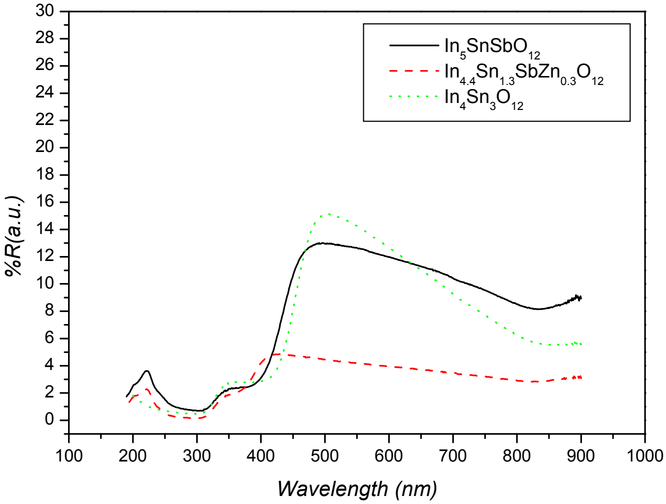


Fig. 3. Measured optical reflectance spectra in the compositions x = 0 (In_5SnSbO_{12} treated at 1400C °C), x = 0.3 (1350 °C) and compared to $In_4Sn_3O_{12}$ (1400 °C).

Electrical resistivity measurements were carried out by the four probe method at room temperature (RT) on pellets sintered at 1350 °C in air. For these experimental conditions, three samples corresponding to compositions x = 0.1, 0.2 and 0.3 were explored. For reference, two sample of $In_4Sn_3O_{12}$ and $In_5SnSbO_{12,}$ sintered at 1400 °C, were also considered. The resistivity values (Table 2) show a decrease of the resistivity for x = 0.1 composition, by approximately one order of magnitude, if compare to $In_4Sn_3O_{12}$. For x = 0.2 and x= 0.3 compositions, introduction of couple Sn/Zn in the presence of Sb does not triggers increase of electrical resistivity, as shown in Table 2. These values are less than one magnitude order if compare with those reported for $In_4Sn_3O_{12}$ by several authors [2, 12, 13]. Thus, the resistivity of the new oxide $In_{4.4}Sn_{1.3}SbZn_{0.1}O_{12}$ is approximately one order of magnitude smaller than that of $In_4Sn_3O_{12}$ and less than one order of magnitude larger than that of In_5SnSbO_{12}.

Table 2. Room temperature electrical resistivity values measured for x= 0.1, x = 0.2 and x = 0.3 compositions belonging to $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system (1350 °C), and compared to In_5SnSbO_{12} and $In_4Sn_3O_{12}$ (1400 °C).

Composition	x = 0 [6]	x = 0.1	x = 0.2	x = 0.3	$In_4Sn_3O_{12}$ [2,12,13]
ρ_{RT} (Ω.cm)	2.8×10^{-3}	5×10^{-3}	9×10^{-2}	6×10^{-2}	$2 - 2.6 \times 10^{-2}$

CONCLUSIONS

The compositions x = 0.1, x = 0.2 and x = 0.3, belonging to $In_{5-2x}Sn_{1+x}SbZn_xO_{12}$ system, have been successfully synthesized by solid state reaction in air. Structure calculations performed by Rietveld analysis of the X-ray powder diffraction (XRPD) data revealed a ordered cationic distribution over the two cationic sites. For $In_{4.4}Sn_{1.3}SbZn_{0.3}O_{12}$ composition a small amount of unreacted SnO_2 was identified. By increasing temperature from 1300 °C to 1350 °C, a decrease of secondary phase amount, from 5.76 wt% to 3.17 wt%, was evidenced. The optical spectra show their potential as transparent conductor. The electrical conductivity of the x = 0.1 composition was enhanced by approximately one order of magnitude with respect to $In_4Sn_3O_{12.}$

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