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# Structural and Physical Property Analysis of $ZnO-SnO_2-In_2O_3-Ga_2O_3$ Quaternary Transparent Conducting Oxide System

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The increasing demand in the diverse device applications of transparent conducting oxides (TCOs) requires synthesis of new TCOs of n- or p-type conductivity. This article is about materials engineering of $ZnO-SnO_2-In_2O_3-Ga_2O_3$ to synthesize powders of the quaternary compound $Zn_{2-x}Sn_{1-x}In_xGa_xO_{4-\delta}$ in the stoichiometry of $x = 0.2$, 0.3, and 0.4 by solid state reaction at 1275 °C. Lattice parameters were determined by X-ray diffraction (XRD) technique and solubility of $In^{3+}$ and $Ga^{3+}$ in spinel $Zn_2SnO_4$ was found at 1275 °C. The solubility limit of $In^{3+}$ and $Ga^{3+}$ in $Zn_2SnO_4$ is found at below $x = 0.4$. The optical transmittance approximated by the UV−Vis reflectance spectra showed excellent characteristics while optical band gap was consistent across 3.2 eV with slight decrease along increasing $x$ value. Carrier mobility of the species was considerably higher than the older versions of zinc stannate spinel co-substitutions whereas the carrier concentrations were moderate.

**KEY WORDS: Transparent conducting oxides (TCOs); Structural studies; Mobility; Optical properties**

## 1. Introduction

The oxides of In, Zn, Sn, and Cd are established widely as the architectural components of new generation transparent conducting electrodes when they are mixed together or substitutionally doped with other metal oxides[1−5]. List of class of transparent conducting oxides (TCOs) is huge because of their extended applications in different types of devices such as organic light-emitting diodes (OLEDs), automobile windows, flat panel displays and photovoltaic devices. For diverse device applications, it is extremely important to prepare various new types of TCOs of n- or p-type conductivity[6−8], with superior optical characteristics, possessing improved work function, morphology, long term stability, elemental abundance, non-toxicity with high annual production rate[9−11]. The best-known materials for commercialized TCOs are based on cations with completed *d*-shells, like $Zn^{2+}$, $Cd^{2+}$, $In^{3+}$, and $Sn^{4+}$, which exhibit n-type character. Binary cation materials like $CdSnO_3$, $ZnSnO_3$, $Zn_2SnO_4$ and ternary cation TCOs $Zn_{2-x}Sn_{1-x}In_{2x}O_4$ and $In_{2-2x}Sn_xZn_xO_3$ exhibit n-type electrical conductivity[12]. However in these systems the electronic transport mechanism appears to be complex but the performance was good in the case of electron mobilities, which was ~50 $m^2/(V\ s)$[13]. Traditionally, the mobility of TCO thin films has been enhanced by improving the crystalline structure by means of heat treatment, deposition technique, choice of substrate and novel materials. Here, the manuscript reports the synthesis and the studies of multinary TCOs derived from the quaternary combination of $ZnO-SnO_2-In_2O_3$ and $Ga_2O_3$. Reports on solid solutions of such combinations claiming much higher performance due to the addition of elements to modify defect and electronic band structure have been made[14]. Structural, electrical, and optical properties of the compound were also investigated. Such TCOs are expected to possess higher mobility of charge carriers than the existing ones[2] with the possibility of variation of stoichiometry, which may serve as a versatile tool for controlling the material's properties.

## 2. Experimental

The powders of $Zn_{2-x}Sn_{1-x}In_xGa_xO_{4-\delta}$ were synthesized by mixing the appropriate quantities of ZnO, $SnO_2$, $In_2O_3$, and $Ga_2O_3$ for $x = 0.2$, 0.3, and 0.4. The samples were of 99.99% purity cation based, purchased from Sigma Aldrich Chemical Co., USA. The initial process of the experiment is to mix the weighed individual powders with an agate mortar and pestle. The mixed powders were coaxially pressed and pellets were loaded

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into a pre-cleaned alumina cylindrical crucible, which can withstand processing at high temperature up to 1700 °C. The crucibles were covered by a tight-fitting alumina lid. The pellets were calcined initially at 1000 °C for 10−12 h and pellets were reground for uniformity, repelletized, and loaded back into the furnace for densification. This process was carried out at a firing temperatures of 1200 °C for 20−24 h, 1250 °C for 20−24 h and ended at 1275 °C for 20−24 h; the longer heating time intended to ensure the phase purity. The structural profile was investigated by X-ray diffraction (XRD) technique with Cu$K\alpha$ radiation, with slow scanning rate in the Bragg angle range of 10−60°. Along with the phase determination the critical parameters including peaks fitting to the reflections, lattice constant and crystallite size were also calculated. PowderX and ICDD software database was used for the assignment of lattice reflections and structural determinations. UV−Vis reflectance spectroscopy was used for the optical characterization of samples. All spectra were taken at room temperature in the range of 325−600 nm on a Lambda-350 Perkin-Elmer spectrometer with an integrating sphere diffuse reflectance accessory. The spectrophotometer measures reflectance relative to a background scatterer. Diffuse reflectance measurements on bulk samples were roughly analogous to transmission measurements on thin films. The data from the reflectance spectra was used to approximate the optical band gap, the absorption edge onset[15] and the Kubelka−Munk[16] theory was used for it. Mobility of the charge carriers and bulk conductivity have been measured by Van der Pauw method[17] using four point Hall setup. As the shape, size and thickness of the specimen are important in the measurements, the samples were in the form of square type pellets densified at high temperature. Simple ohmic contact from silver adhesive paste was used to measure current and voltage dependence for the material.

## 3. Results and Discussion

### 3.1. Structural and phase determination

Fig. 1 shows the over layered powder XRD patterns of the species with chemical formula $Zn_{2-x}Sn_{1-x}In_xGa_xO_{4-\delta}$ in the solid solution range of $x = 0.2$, 0.3, and 0.4 at 1275 °C. Table 1 shows the lattice parameters and crystallite size calculated from the XRD data. The dominant peaks of each pattern are used for structural parameter calculations. The average grain size of the solid solutions can be determined from the corresponding X-ray spectral peaks by Scherrer formula[18].

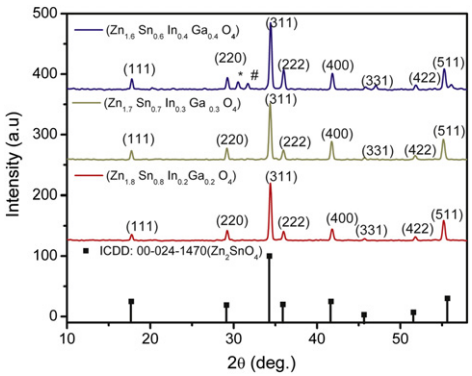


**Fig. 1** Combined XRD plots of $Zn_{2-x}Sn_{1-x}In_xGa_xO_{4-\delta}$ at ($x = 0.2$, 0.3, 0.4), exhibiting cubic spinel phase with reduced solubility of $In_2O_3$ indicated by (*) and $Ga_2O_3$ by (#) for $x = 0.4$.

**Table 1** Lattice constant $a$, crystallite size and $d$-spacing calculated from the dominant (311) reflection of the individual XRD plots

| Sample | $2\theta$ (deg.) | $d$ (nm) | Crystallite size (nm) | Lattice constant $a$ (nm) |
|---|---|---|---|---|
| $Zn_{1.8}Sn_{0.8}In_{0.2}Ga_{0.2}O_4$ | 34.45 | 0.26019 | 268.33 | 0.86296 |
| $Zn_{1.7}Sn_{0.7}In_{0.3}Ga_{0.3}O_4$ | 34.28 | 0.26144 | 184.83 | 0.86491 |
| $Zn_{1.6}Sn_{0.6}In_{0.4}Ga_{0.4}O_4$ | 34.41 | 0.26048 | 202.90 | 0.86393 |

Analysis of XRD picture (Fig. 1) shows that the crystal structures for $Zn_{1.8}Sn_{0.8}In_{0.2}Ga_{0.2}O_{4-\delta}$ ($x = 0.2$) and $Zn_{1.7}Sn_{0.7}In_{0.3}Ga_{0.3}O_4$ ($x = 0.3$) can be identified to be similar in structure to that of the cubic spinel phase of $Zn_2SnO_4$ (ICDD: 00-024-1470) with reduced solubility of $In^{3+}$ and $Ga^{3+}$ for $x = 0.40$. From this aspect, the structural phase purity and phase determination studies can be further split into two: ternary phase $Zn_2SnO_4$ and quaternary phase $Zn_2SnO_4$−$In_2O_3$−$Ga_2O_3$. Also, it can be found that the compositions with stoichiometry of $x = 0.2$ and 0.3 show similar XRD spectra with a negligible variation in the lattice parameters and crystallite size. The assignments on the indices are indicated in Fig. 1, which is confirmed and calculated through PowderX. As assigned previously, the structure of the specimen is shown in the inverse cubic $c$ phase with a face centered cubic (fcc) unit cell. In $Zn_2SnO_4$, the $Sn^{4+}$ ions are located in octahedral coordination whereas 50% of the $Zn^{2+}$ ions are in octahedral coordination and the rest ones are in tetrahedral coordination[10]. The final material in this synthesis corresponds to the chemical formula $Zn_{1.8}Sn_{0.8}In_{0.2}Ga_{0.2}O_{4-\delta}$ and $Zn_{1.7}Sn_{0.7}In_{0.3}Ga_{0.3}O_{4-\delta}$. There are no peaks in the XRD spectra corresponding to either $In_2O_3$ or $Ga_2O_3$. This is due to the substitutional incorporation of $In^{3+}$ and $Ga^{3+}$ in the spinel zinc stannate lattice. Harvey et al.[9] previously illustrated the inverse spinel face centered cubic In substituted $Zn_2SnO_4$ transparent conductors. Extra lines observed from the third sample for $x = 0.4$ is due to the presence of cubic ($In_2O_3$) and monoclinic ($Ga_2O_3$)[19,20]. This is a substantiating evidence of negligible solid solubility of $In_2O_3$ and $Ga_2O_3$ in the $Zn_2SnO_4$ matrix. Increasing the firing time and temperature requires producing the single-phase spinel $Zn_{2-x}Sn_{1-x}In_xGa_xO_{4-\delta}$ with increasing $x$.

From the X-ray reflection of (311) the predominant peak is used to construct Table 1. In the inverse, cubic spinel crystals of $Zn_2SnO_4$ with substitutional In and Ga lattice constants are found to increase with $x$ for every 0.1 step. This finding is consistent with results of Moriga et al.[10], which also reported the increase of the lattice constant due to the incorporation of $In^{3+}$. The relatively small changes in lattice constants are the consequence of the similarity of the ionic radii of $In^{3+}$ and $Ga^{3+}$ as well as of $Sn^{4+}$ and $Zn^{2+}$. Table 1 shows the observed and calculated lattice parameters and crystallite size of the specimens estimated from the XRD pattern.

### 3.2. Optical measurements

The information about the optical properties of the synthesized powders have been obtained by measurements using the UV−Vis spectra in reflectance modes, which are analogous to transmittance spectra and allow to perform comparisons with transmission spectra for films. Fig. 2 shows the reflectance spectra measured in the wavelength range of 300−600 nm. Transport