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A Detailed Study on the Structural, Electrical and Optical Properties of $(ZnO\text{-}GeO_2)$ Substituted In_2O_3 Transparent Conducting Oxide

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Abstract

In this study, ZnO and GeO_2 substituted In_2O_3 ternary system is investigated with various characterization methods for optical, electrical and structural properties. This new transparent conducting oxide prepared different composition which can be symbolized as $Zn_xIn_{2-2x}Ge_xO_3$ $0.1 \leq x \leq 0.5$. The optical properties of the samples obtained show that the optical band gap enhances from 2.94 eV to 3.16 eV with the augmentation of the x value. Conductivity values for $x = 0.1$ is about 308 S/cm and 1060 S/cm for unreduced and reduced samples respectively. The reduced conductivity of $Zn_{0.476}In_{1.032}Ge_{0.476}O_3$ is about 135 S/cm and for this composition samples are phase pure for new fluorite related phase. Thus, this study stresses the importance of cosubstitution to decrease amount of indium and understanding the various results for bulk samples.

Keywords: Zn and Ge substitution, Transparent Conducting Oxide, $ZnO\text{-}In_2O_3\text{-}GeO_2$ system, XRD

1. INTRODUCTION

In the past decade, significant development and innovation has been made on Transparent Conducting Oxide (TCO) due to its importance on building various devices like flat panel display and photovoltaic devices [1, 2]. The reason for this intense interest in TCOs is because of the fact that TCOs are degenerately doped semiconductor and highly transparent to visible radiation. So, these features allowed them to be used in future technologies. There are couple well known TCOs including In_2O_3:Sn (ITO), SnO_2:F and ZnO:Al [3, 4]. Among those of well known TCOs, ITO is the most widely used transparent conducting oxide material. However, Indium is a scarce metal and it is very expensive and low resource, researchers has been seeking for new TCOs to decrease the Indium content of its. Last two decades, many research groups have been searching for cosubstitution [5]. For that purpose, two relatively cheaper materials have been chosen as constituent. As Freeman et al. [6] suggested, there are many novel compound and solid solution ceramic TCOs are not discovered. It has been decided that (2-3-4) ternary system which has Zn^{+2} divalent, In^{+3} trivalent and Ge^{+4} tetravalent to obtain new bulk phase. For this reason, ZnO and GeO_2 has been choosen as constituent to the In_2O_3. In the ternaries phase space with (2-3-4) ternary system have shown B and S phase so far. There was not any T space for that system. In this study Zn^{+2} and Ge^{+4} substituted into In_2O_3 and new phase space transformation for this special ternary system. This new phase has been identified as T-phase because of its tetragonal structure. There are some research groups who studied Ge doped In_2O_3 and Ge and Zn codoped In_2O_3. They have reported that Ge^{+4} doped In_2O_3 has very small solubility about 1%-1.5%, and there was observed secondary phases which affected sample densification and electric

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conductivity negatively [7]. For Ge^{+4} and Zn^{+2} codoped system has been reported as very suitable for thermoelectric materials and has very high electric conductivity which has decreased with increasing doping concentration. Moreover, in this system, they observed GeO_2 is the secondary phase and there was not any evidence for the new ZIGO structure [8]. Before understanding of new phase, we should mention about ZnO-In_2O_3-GeO_2 system which has three oxides and each of these oxides crystallizes different way. To clarify, In_2O_3 has bixbyite crystalline structure which can be seen as distorted fluorite structure with missing anions from b site or d site and has space group (Ia_3) [9]. GeO_2 has isostructural rutile structure with space group ($P4_2/mnm$) [10]. ZnO has tetrahedral wurtzite structure, where Zn^{+2} and O^{-2} coordinated by four Zn^{+2} and O^{-2} respectively and have a space group ($P6_3mc$) [11].

2. EXPERIMENTAL DETAILS

All ZIGO samples were synthesized by high temperature solid state reaction method. The starting materials to synthesize bulk ceramic were commercial oxide powders of GeO_2 (99.99% Sigma Aldrich), In_2O_3 (99.99% Alfa Aeser) and ZnO (99.99% Sigma Aldrich). The new bulk ceramic which can denote as $Zn_xIn_{2-2x}Ge_xO_3$ for $0.1 \leq x \leq 0.5$ and stoichiometry of the samples are given in the Table 1. GeO_2, In_2O_3 and ZnO powder were weighted carefully with sensitivity about 1 milligram. All powders are mixed into agate mortar stoichiometrically and grinded about 10 minutes. After that, they were ground under acetone and put into drying oven. Then, dried mixture grinded again and pressed into a pellet with 13 mm diameter. Sacrificial powders were placed into the small alumina crucible then pressed pellet buried in same composition of sacrificial powder. Small crucible capped a lid and put into the bigger crucible. This method was thought as necessary to prevent Zn volatilization and keep reaction isovalent [12, 13]. Samples were sintered at a furnace programmed as heating 20 °C per minute to temperature 1250 °C dwelled at this temperature for 16h and cooled down to room temperature 10°C per minute. X-ray powder diffraction analysis of ZIGO was performed at room temperature in the angular range of $2\theta = 20° - 70°$ with scan step of 0.1° and a continuous counting time of 4° per minute using an automated Rigaku X-Ray diffractometer equipped with Cu kα radiation of wavelength $\lambda = 1.5418$ Å.

Table 1 The Composition of ZnO, In_2O_3 and GeO_2 ternary system

Name	ZnO	GeO_2	In_2O_3	Formulization
ZIGO10	10%	10%	90%	$Zn_{0.1}In_{1.8}Ge_{0.1}O_3$
ZIGO20	20%	20%	80%	$Zn_{0.2}In_{1.6}Ge_{0.2}O_3$
ZIGO30	30%	30%	70%	$Zn_{0.3}In_{1.4}Ge_{0.3}O_3$
ZIGO40	40%	40%	60%	$Zn_{0.4}In_{1.2}Ge_{0.4}O_3$
ZIGOB	48.39%	48.39%	51.61%	$Zn_{0.476}In_{1.032}Ge_{0.476}O_3$
ZIGOC	47.62%	47.62%	52.38%	$Zn_{0.484}In_{1.048}Ge_{0.484}O_3$
ZIGO50	50%	50%	50%	$Zn_{0.5}In_{1.0}Ge_{0.5}O_3$

For being certain, PXRD measurement has been repeated with crystalline silica standard. In this way, device errors have been eliminated and calibration standard of peak positions in PXRD have been ensured. The Perkin Elmer 1050 UV-Vis-NIR spectrometer with Lambda 150 nm integrated sphere accessory allowed diffuse reflectance measurement are used for optical characterization of samples which has been measure wavelength between 300-800 nm. Electrical conductivity measurement of pellets were taken at room temperature in four point probe geometry configuration [14, 15].

3. RESULTS and DISCUSSIONS

In Figure 1 and 2, XRD pattern of sintered ZIGO samples have been showed. The XRD showed clearly the evolution of new phase. ZIGO10 showed highly dominated bixbyite phase. Bixbyite 222 peak and adequately big new phase most dominant peak can be seen at 30.763° (bixbyite 222) and 31.283° respectively. While further decreased In_2O_3 concentration in the samples, bixbyite phase was disappeared, and new phase diffraction peaks became dominant. Increasing concentration of ZnO and GeO_2 shows Ge and Zn became structural elements rather than substitutional one. $Zn_{0.476}In_{1.032}Ge_{0.476}O_3$ is the exact formulation of new $ZnO-In_2O_3-GeO_2$ system [16]. According to formulization, about 47% molar percent of Indium has removed from samples. For this sensivity of PXRD results $Zn_{0.476}In_{1.032}Ge_{0.476}O_3$ formulation does not show any secondary phases. It has not been indexed with any discovered $ZnO-In_2O_3-GeO_2$ bulk system or reaction with alumina crucible. However, Rickert et al. [17] indexed that $Zn_{0.456}In_{1.084}Ge_{0.460}O_3$ (ZIGO) contained three phases and this new phase not related to bixbyite on the contrary it is fluorite related tetragonal phases. The product of high temperature samples exhibited XRD pattern with peak characteristic tetragonal phase structure. Major peaks of this phase are similar to bixbyite which is to be expected as lanthanides and actinides form various fluoride related phases. PXRD results with Silica standard are used to determine exact position of diffraction patterns. So diffractograms with and without Silica standard illustrate several interesting features regarding to new system consequently [18]. Firstly, any thought of the new diffraction peaks is the shifts of bixbyite phase are refuted because of Silica standard PXRD peaks. Secondly, it can comfortably say that while looking these four most intense peaks of bixbyite structure disappear via increasing Zn^{+2}/Ge^{+4} composition. In other word, bixbyite phase disapper by adding Zn^{+2}/Ge^{+4} substitutions.

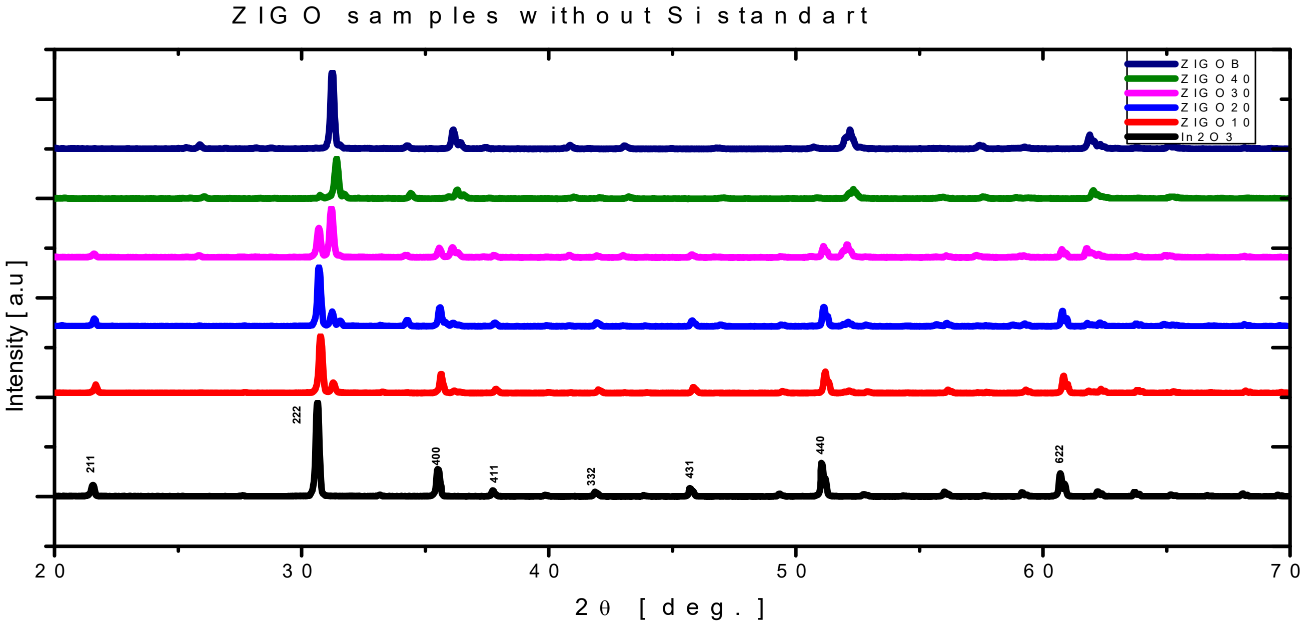

Figure 1 PXRD results of Zn-In-Ge-O ternary system without Silica standard. Black plots represent bixbyite hkl indexes (colored)

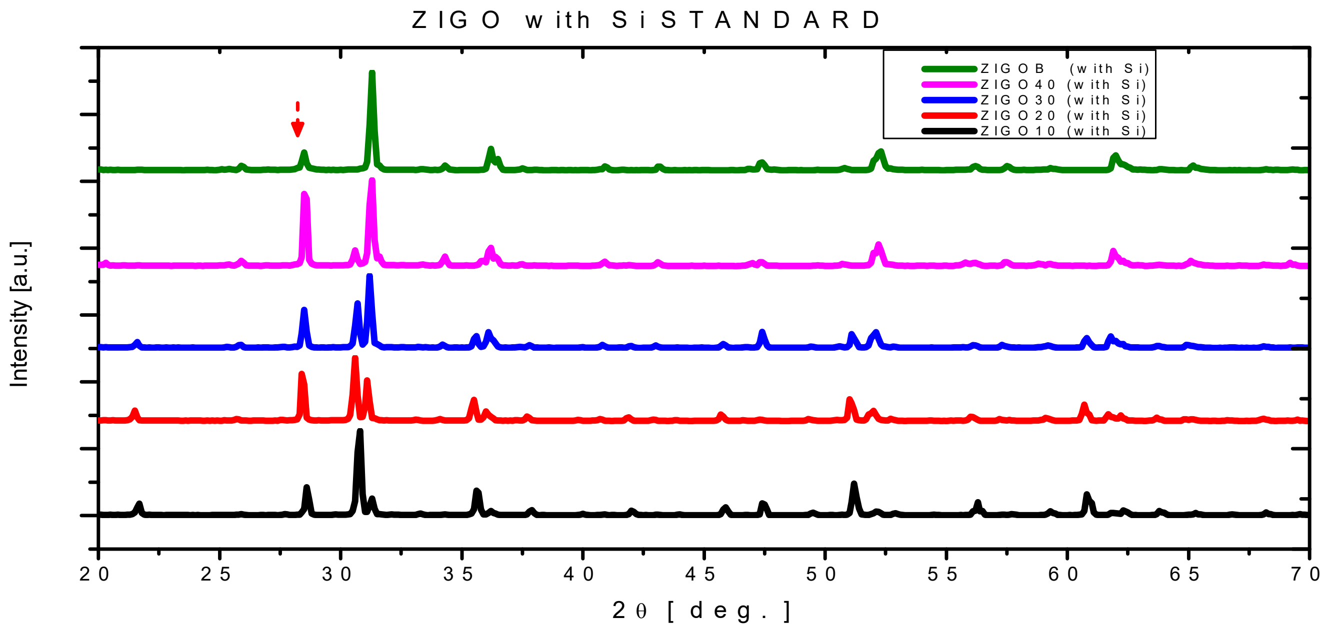

Figure 2 PXRD results of Zn-In-Ge-O ternary system with Silica standard (Red arrow indicates (111) Si internal standard peaks in samples) (colored)

All the prepared samples in this study have been plotted by composition in the Figure 3. In Figure 3, edges are $ZnO-In_2O_3-GeO_2$ and it is seen in the Figure 3 that $ZnO-GeO_2$ ratio was kept equal for all [5] . Further experiment can be conducted to fill empty space in Figure 3. In the binary system $ZnO-In_2O_3$ and $In_2O_3-GeO_2$, just one binary compound cubic bixbyite was reported in perevious studies [7, 8, 19].

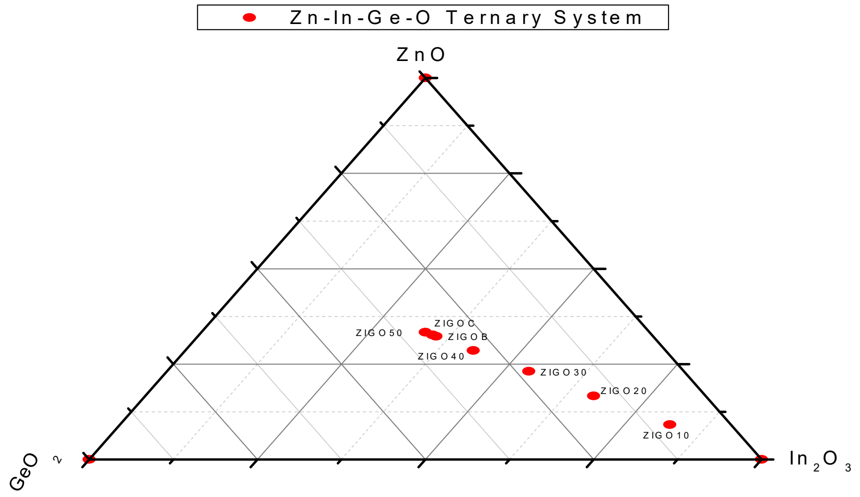

Figure 3 Subsolidus phase relations in Zn-In-Ge-O system (colored)

Electrical conductivity of reported ternary system as a function of In^{+3} content is given in Figure 4 and porosity corrections are made by the Bruggemann symmetric model [14]. The electrical conductivity of pellet samples for $Zn_{0.1}In_{1.8}Ge_{0.1}O_3$ composition is 308 S/cm and 1060 S/cm for unreduced and reduced samples respectively. The reduced conductivity of $Zn_{0.476}In_{1.032}Ge_{0.476}O_3$ decreased up to 135 S/cm [17, 20-22]. Conductivity results indicate that this new system has similar conductivity behavior of other In_2O_3 based ternary system [21, 22].

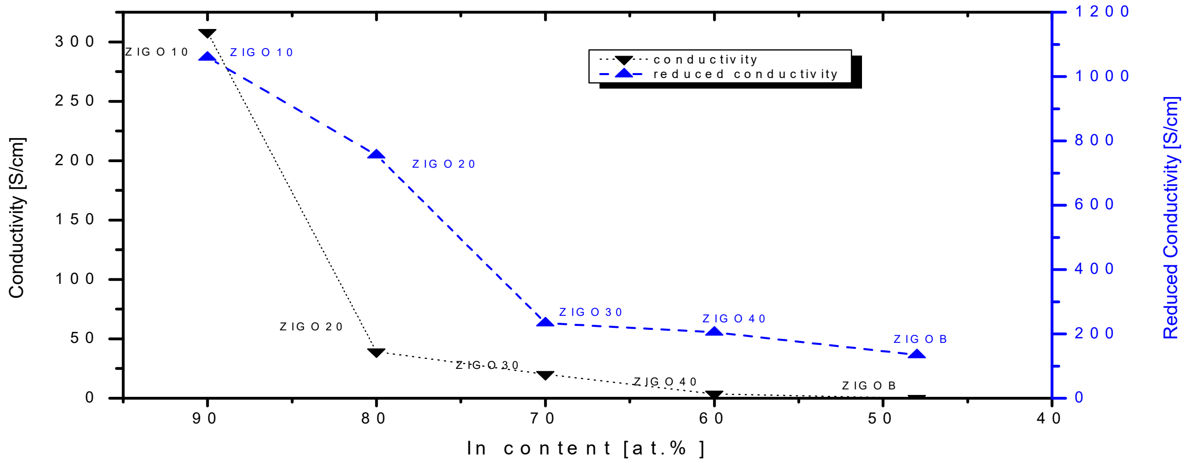

Figure 4 Reduced and unreduced electrical conductivity of ZIGO samples (colored)

Reduced and unreduced samples conductivity is increasing with the decrement of ZnO and GeO_2 substitution regard to In_2O_3. This result shows that new phase ZIGO system has not superior electric properties with respect to ITO [23]. For conductivity point of view, it should be note that composition and conductivity properties look similar with ITO. As mentioned above, samples stoichiometry can be denoted as $Zn_xIn_{2-2x}Ge_xO_3$ $(0.1 \leq x \leq 0.5)$ and for increasing ZnO and GeO_2 substitution regard to In_2O_3 has increased optical band gap of new materials owing to substitutions wide band gap [24]. Samples optical band gap estimated with Kubalka Munk function [25] is given below

$$F(R_\infty) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \qquad (1)$$

where K-M are the absorption and scattering coefficient respectively and R_∞ is reflectance of specimen. The absorption coefficient in the equation 1 can be related to the optical band gap with Tauc equation [26] as written below

$$\alpha h\nu = C_1 (h\nu - E_g)^\gamma \qquad (2)$$

$$(\alpha h\nu)^{\frac{1}{\gamma}} = C_2 (h\nu - E_g) \qquad (3)$$

Samples conductivities are 2.94 eV, 2.99 eV, 3.05eV, 3.14 eV and 3.16 eV for x= 0.1, 0.2, 0.3, 0.4 and 0.456 respectively. The fundamental absorption edge for given composition is around 400 nm similar to In_2O_3 [27]. By adding substitutant into sample, optical bandgap shifted the larger energies and reflectance shifted to lower wavelength [28].

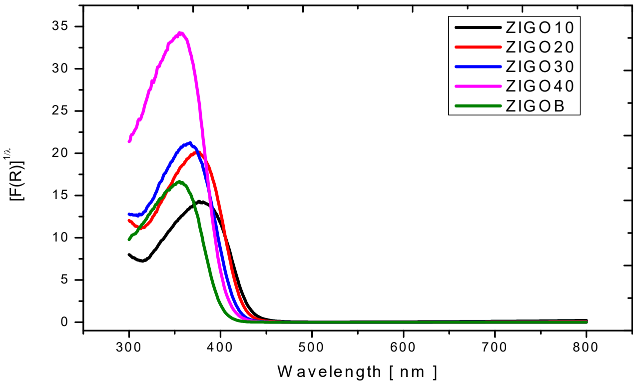

Figure 5 F(R) versus wavelength spectra of various compositions (colored)

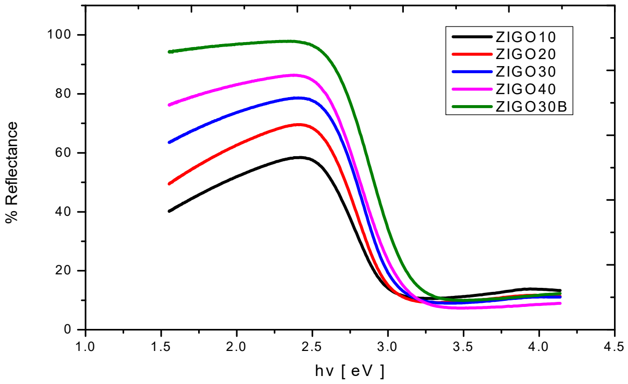

Figure 6 Diffuse Reflectance versus hv spectra of various compositions (colored)

4. CONCLUSION

It has been presented that ZnO and GeO_2 cosubstituted regard to In_2O_3 are very promising replacement to for ITO. Here phase relation of ZnO-In_2O_3-GeO_2 system has been established successfully. ZIGO has less amount of In_2O_3 than ITO which decreases the cost of this system dramatically. New TCO contains 47% less indium. However electronic properties of ZIGO have not succeeded ITO's electronic properties. Thin films studies must be conducted on this system. Pure phase ZIGO has band gab 3.16 eV. The phase diagram of this system is shown in Figure 3. Excess amount of Zn^{+2} and Ge^{+4} studies could be a suitable alternative for carrier mechanism and can break new ground on conductivity properties of this new system.

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