

Zinc Doping in Cosubstituted $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$

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The cosubstituted solid solution $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$ was acceptor-doped with Zn^{2+} to form $\text{In}_{2-x-y}\text{Sn}_x\text{Zn}_y\text{O}_{3-\delta}$ ($y > x$). A 4% Zn^{2+} “excess” can be introduced in $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ while maintaining the bixbyite structure. The n-type conductivity of the doped material decreases with zinc substitution. Zn-doped $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ was annealed under high oxygen pressure (~ 170 atm) to eliminate anion vacancies, $\text{V}_\text{O}^\bullet$. Owing to a decrease in carrier concentration by up to 2 orders of magnitude from 10^{20} to 10^{18} carriers/cm³, the conductivity of the annealed material decreases. Hall measurements show that the carriers remain as n-type. The results imply the existence of neutral $\text{Zn}-\text{V}_\text{O}^\bullet$ complexes that prevent the donation of holes by Zn^{2+} .

Introduction

Transparent conducting oxides (TCOs) are widely used as transparent electrodes in a variety of technological applications such as solar cells and flat panel and liquid crystal displays. Sn-doped indium oxide (ITO) is currently the most widely used TCO, as it exhibits conductivities on the order of 10^3 S/cm and is over 85% transparent in thin film form.^{1–5} ITO as well as other industrially useful TCOs are n-type degenerate semiconductors with delocalized dopant levels which overlap the conduction band.

In_2O_3 and ITO are generally nonstoichiometric with respect to oxygen, leading to the formula $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-\delta}$. Delta (δ) is influenced by synthesis conditions and dopant concentration and can be as high as 0.01 in undoped indium oxide.⁶ Oxygen nonstoichiometry contributes two electrons per oxygen vacancy. However, in ITO, the number of carriers generated by doping with Sn^{4+} far outnumbers that due to nonstoichiometry and

is responsible for the high conductivity of the material.^{7,8} In addition, the substitution of In^{3+} by Sn^{4+} can decrease the value of δ , as oxygen will often be incorporated into the structure as a charge-compensating anion.⁹

In_2O_3 can be substituted with up to 6–8% of SnO_2 before a second phase is formed.^{10–12} Zinc oxide, ZnO , which forms a series of layered compounds with In_2O_3 , has an even lower solid solubility than SnO_2 (less than 2%).^{13,14} However, when equal amounts of Sn^{4+} and Zn^{2+} are simultaneously codoped in In_2O_3 , their respective solubilities can be increased greatly. The resulting solid solution, $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$, can extend to $x = 0.4$.¹⁵ The reason for this increased solid solubility lies in the isovalent substitution of a Sn^{4+} cation and a Zn^{2+} cation for a pair of In^{3+} cations, thereby maintaining charge neutrality. Despite the fact that this material is isovalently substituted, $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$ displays n-type conductivity, owing to the presence of anion vacancies represented by δ .

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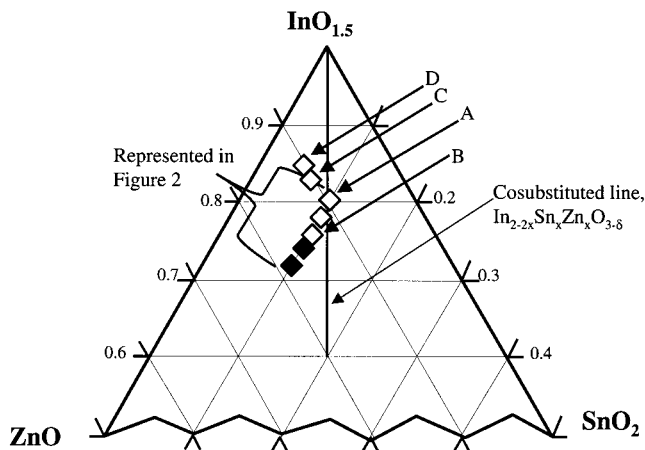


Figure 1. Partial phase diagram of the In-Sn-Zn system. The points represent the stoichiometries of the synthesized samples. The open diamonds indicate single-phase samples while the closed diamonds refer to biphasic samples.

Table 1. Representative Samples in the Zn-Doped Solid Solution Area^a

composition	% $[\text{Zn}]_{\text{excess}}^b$	point in Figure 1
$\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$	0	A
$\text{In}_{1.58}\text{Sn}_{0.2}\text{Zn}_{0.28}\text{O}_{3-\delta}$	4	B
$\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$	2	C
$\text{In}_{1.68}\text{Sn}_{0.12}\text{Zn}_{0.2}\text{O}_{3-\delta}$	4	D

^a Labels correspond to points in Figure 1. ^b Excess Zn refers to the amount of Zn not compensated by Sn, i.e., $[\text{Zn}] - [\text{Sn}] = [\text{Zn}]_{\text{excess}}$.

Investigations were conducted into the extent of the solid solution in the In_2O_3 - SnO_2 - ZnO system. Little is known about the effects and extent of doping the solid solution with excess Zn^{2+} and whether such doping will generate hole carriers. In this paper, the structural, optical, and electrical properties of Zn^{2+} -doped $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$ are discussed.

Experimental Section

Figure 1 illustrates the cosubstituted region of the In_2O_3 - SnO_2 - ZnO oxide phase diagram. The points in Figure 1 represent the stoichiometries of the samples synthesized in this investigation. Table 1 relates specific compounds that are discussed in this paper to their locations on the phase diagram.

Atomic percentages and concentrations are on a cation basis. Stoichiometric amounts of In_2O_3 , SnO_2 , and ZnO (Aldrich or Alpha Aesar, 99.99% cation purity) were weighed and thoroughly ground with an agate mortar and pestle. Acetone was used as a moistening agent. After the evaporation of acetone, the samples were uniaxially pressed under 7–8 MPa. The pellets were placed in covered alumina crucibles, heated for 2–4 days at 1100 °C, reground and repelletized, and heated at 1250 °C for 1–3 days. To prevent contamination from the alumina crucible and to minimize vaporization, the pellets were buried in a bed of sacrificial powder of the same chemical composition.

A sample of the composition $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, C) was oxidized in a high oxygen pressure furnace (Morris Research) at 750 °C and oxygen pressure of 170 atm. Alternatively, a sample of composition $\text{In}_{1.68}\text{Sn}_{0.12}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, D) was treated under 2 GPa of pressure for 30 min at 600 °C.¹⁶ KClO_4 was used as an oxidizing agent. All of the as-fired compounds were green in color but lightened with increasing zinc substitution. The materials turned bright yellow after oxidation.

X-ray powder diffraction patterns, used to determine reaction completion and phase identification, were recorded on a

Rigaku diffractometer (Cu $\text{K}\alpha$ radiation, Ni filter, $2\theta = 10$ – 70° , 0.05° θ /step, and 1 s counting time). The Jade 5 XRD pattern processing program¹⁷ was used to calculate lattice parameters by pattern matching. The FullProf pattern refinement program¹⁸ was used to further refine the data of selected powder patterns. Si powder (JCPDF #27-1402)¹⁹ was added to some samples as an internal standard to correct off-axis shifts (2θ).

Room-temperature conductivity was measured with a linear, spring-loaded four-probe apparatus by using a Keithly current source and voltmeter (models 225 and 197, respectively). Correction factors from Smits²⁰ were used to adjust for the geometry and finite thickness of the disc-shaped pellets. Because the electrical properties of these materials depend heavily upon preparation methods, only samples that were prepared by similar synthesis methods in this lab were compared.

Conductivity and dc Hall measurements were taken from 4.2 to 340 K by using a computer-controlled, five-probe technique.²¹ For the conductivity measurements, the voltage electrodes consisted of 25 μm gold wire, placed approximately 0.5 cm apart. The voltage contacts on the samples were prepared with indium dots and the gold electrode wires were attached to these contacts with silver paste. On these materials, voltage contacts made with indium and silver paste were found to be superior to those made with only gold or silver paste. The current electrodes consisted of 60 μm gold wire and were attached to the ends of the samples with gold paste. Hall measurements utilized magnetic flux densities of 7400 G and applied currents of 100 mA. All voltages were measured with a Keithly 181 nanovoltmeter.

Variable-temperature thermopower measurements were taken by using a computer-controlled slow-ac technique from 4.2 to 295 K.²² During the measurement procedure, the samples were maintained in a 10^{-5} Torr vacuum. The samples were attached with gold paste to two 60 μm diameter gold wires, which were in turn attached to separate quartz blocks with resistive heaters. Temperature gradients of 0.1–0.4 K were applied and measured with Au (0.07% Fe)/chromel differential thermocouples. The voltage electrodes were 10 μm diameter gold wires. The sample and thermocouple voltages were measured with Keithley 181 and Keithley 182 nanovoltmeters, respectively.

Diffuse reflectance was used to determine the optical transmittance of the as-fired and oxidized pellets.²³ A double beam spectrophotometer (Cary 1E with Cary 1/3 attachment, Varian, USA) was used to measure diffuse reflectance of the bulk samples vs a poly(tetrafluoroethylene) (PTFE) standard (Varian part number 04-101439-00), from 200 to 850 nm. The optical data were used to determine the maximum percent transmittance (usually at 500 nm) and to estimate the optical band gap, which is roughly equal to the onset of absorption of the material.

Electron diffraction (ED) was carried out on a Hitachi 8100 electron microscope at 200 kV. Samples were prepared by crushing the sintered material in alcohol. The small crystallites were deposited on a holey carbon film supported by a copper grid. Energy-dispersive X-ray spectroscopy (EDS) analyses were performed on numerous crystallites of the powder

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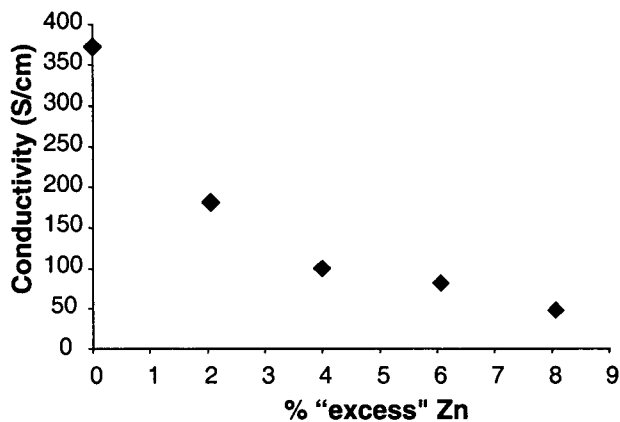


Figure 2. Room-temperature conductivity vs % of excess Zn in $\text{In}_{1.6-x}\text{Sn}_{0.2}\text{Zn}_{0.2+x}\text{O}_{3-\delta}$.

samples with a KEVEX analyzer mounted on the electron microscope.

Results

As-Fired Zn^{2+} -Doped $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$. Indium oxide crystallizes in the cubic bixbyite structure ($Ia\bar{3}$) with a lattice parameter $a = 10.117 \text{ \AA}$ (PCPDF #06-0416).¹⁹ Up to 4% of excess Zn^{2+} ($x = 0.08$) can be substituted into the bixbyite solid solution $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ without the detection of a second phase by XRD and ED. Excess zinc refers to the amount of zinc not compensated by tin, i.e., $[\text{Zn}]_{\text{total}} - [\text{Sn}] = [\text{Zn}]_{\text{excess}}$. The doped compound retains the bixbyite structure, but the lattice parameter decreases as the smaller Zn^{2+} cation is substituted for In^{3+} , from 10.0619(7) \AA for undoped $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ to 10.0596(8) \AA for $\text{In}_{1.6-x}\text{Sn}_{0.2}\text{Zn}_{0.2+x}\text{O}_{3-\delta}$ ($x = 0.08$) (Table 1, B).

A decrease in conductivity is observed as Zn^{2+} substitutes for In^{3+} in the series $\text{In}_{1.6-x}\text{Sn}_{0.2}\text{Zn}_{0.2+x}\text{O}_{3-\delta}$ ($x = 0, 0.04, 0.08, 0.12, 0.16$) in which the concentration of tin was held constant at 10 cationic % (Figure 2). Diffuse reflectance measurements indicate a small increase in transmittance and decrease in optical band gap (from approximately 3.1–2.8 eV) as the concentration of zinc is increased. Conductivity vs temperature measurements of $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, C) show that the material, like its analogous undoped counterpart, behaves as a degenerate semiconductor, although the conductivity is lower (Figure 3). The carrier concentration, taken from Hall measurements, decreases slightly with increased Zn^{2+} doping, from 2×10^{20} to $1 \times 10^{20} \text{ cm}^{-3}$ for undoped $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ and $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$, respectively.

Oxygen-Annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$. A sample of $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, C) that was annealed in the high oxygen pressure furnace changed color from pale green to bright yellow. This color change can be seen in the diffuse reflectance spectra as the optical band gap shifts from 2.95 eV (420 nm) to 2.79 eV (444 nm) (Figure 4). The percent transmittance also increases dramatically after oxidation from 30 to over 80% relative to the PTFE standard. The annealed material retains the bixbyite structure, as seen in powder XRD and ED (Figure 5). A small decrease in lattice parameter occurs upon oxidation, from 10.0711(5) \AA to 10.0694(4) \AA . The postannealed conductivity drops by almost 2 orders of magnitude, while its behavior changes from a

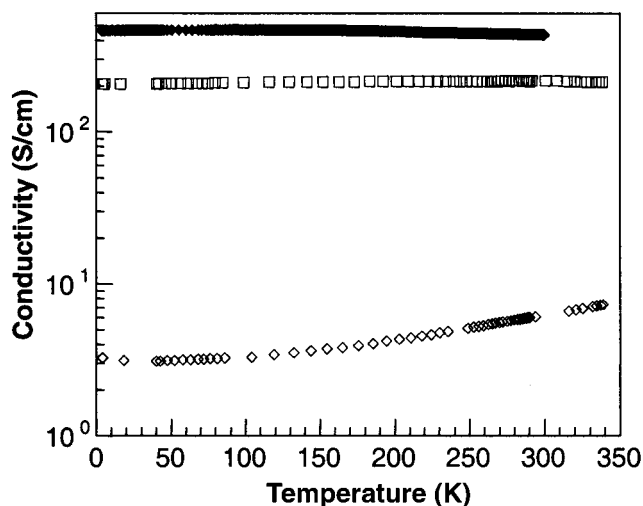


Figure 3. Conductivity vs temperature behavior of (♦) undoped cosubstituted $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$, (□) as-fired $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$, and (◇) high oxygen pressure annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$.

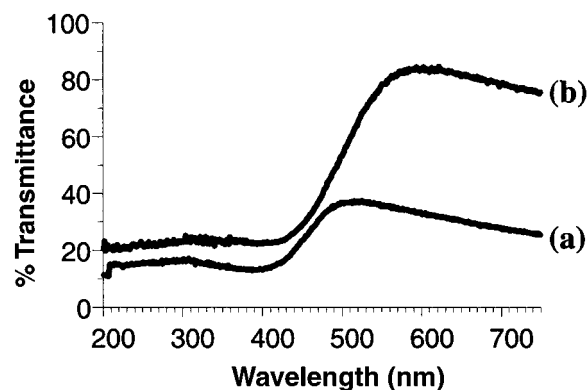


Figure 4. Diffuse reflectance of (a) as-fired and (b) high oxygen pressure annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$.

degenerate to a nondegenerate semiconductor (Figure 3). The carrier concentration also decreases by 2 orders of magnitude, from 10^{20} to $10^{18} \text{ carriers/cm}^3$ (Figure 6a). The carriers in both the as-fired and annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$ are electrons, indicating n-type electrical conductivity. There is a small drop in mobility after the high oxygen pressure anneal (Figure 6b).

High-Pressure Anneal. The compound with formula $\text{In}_{1.68}\text{Sn}_{0.12}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, D) was annealed under 2 GPa of pressure with KClO_4 as an oxidizing agent. The color changed again from green to yellow, and the material retained the cubic bixbyite structure as determined by powder XRD and ED. There was a slight, if any, decrease in lattice parameter after oxidation, from $a = 10.088(3) \text{ \AA}$ to $a = 10.081(6) \text{ \AA}$. While the product was too irregularly shaped to obtain any useful Hall measurement data, it was possible to measure thermopower (Figure 7a) and conductivity from 50 to 300 K (Figure 7b). Thermopower measurements show that the material is n-type, while the conductivity behavior of the sample is similar to that of the high oxygen pressure annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$, although the actual conductivity has decreased to a room-temperature value of 2 S/cm.

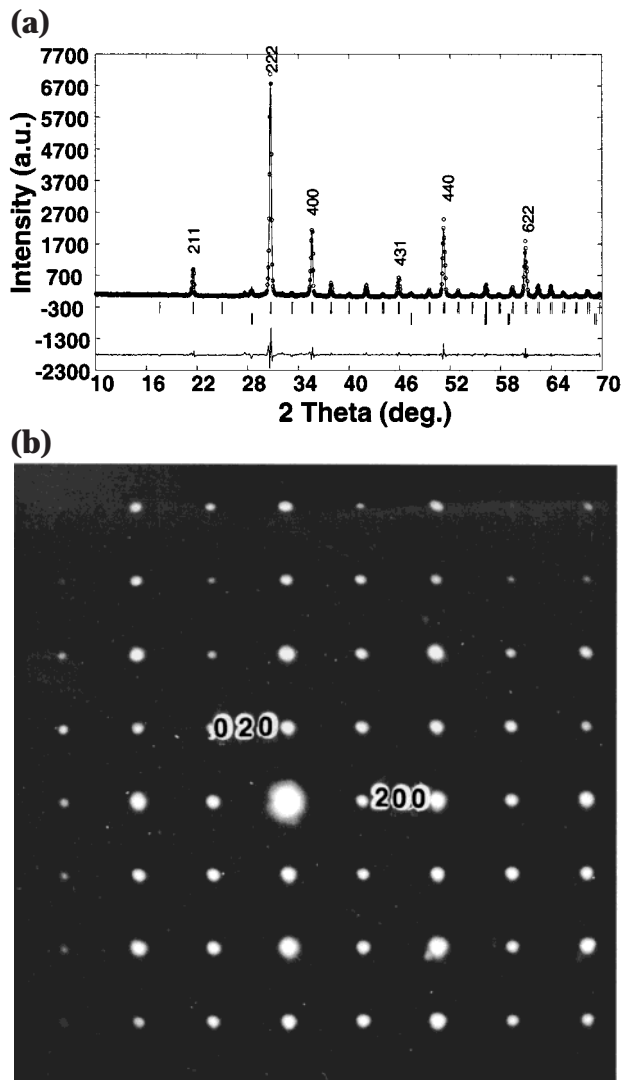


Figure 5. (a) Powder X-ray diffraction pattern of high oxygen pressure annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$ pattern—matched with the use of FullProf. Si powder was used as a standard. (b) Electron diffraction pattern [001] of high oxygen pressure annealed $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$.

Discussion

Moriga et al. previously found that at 1250 °C, the solubility of ZnO in In_2O_3 is less than 2%.¹⁴ However, it is possible to dope up to 4% excess Zn^{2+} into the cosubstituted solid solution with the initial composition $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, A). The decrease in lattice parameter of the bixbyite structure as the zinc concentration is increased indicates that zinc has substituted into the structure. Powder XRD, ED, and EDS support this conclusion. Supposing the formation of a second phase such as $\text{In}_2\text{Zn}_3\text{O}_6$ ($k = 3$)^{13,24} in $\text{In}_{1.52}\text{Sn}_{0.2}\text{Zn}_{0.28}\text{O}_{3-\delta}$ (Table 1, B) went undetected by structural characterization, the conductivity values of the doped sample would still support the conclusion that zinc is substituted into the structure. If a small amount of $\text{In}_2\text{Zn}_3\text{O}_6$ was present, the remaining solid solution would be composed of 78% In, 11% Sn, and 11% Zn, as calculated by drawing a line on the phase diagram between $\text{In}_2\text{Zn}_3\text{O}_6$ and the cosubstitution line through

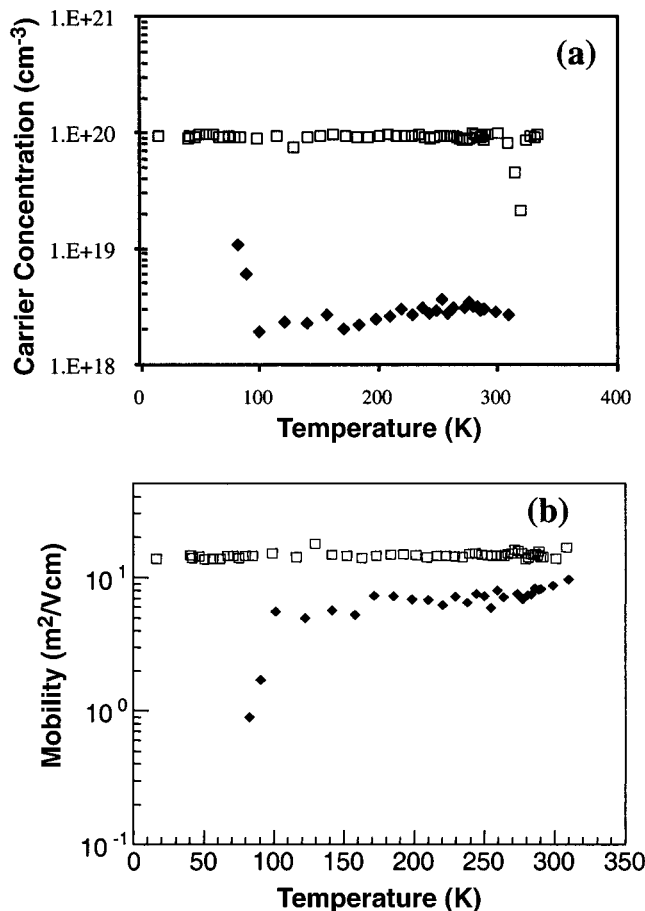


Figure 6. Carrier concentration (a) and mobility (b) vs temperature for $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$, as-fired (\square) and annealed under high oxygen pressure (\blacklozenge).

sample B. From previous work,¹⁵ the conductivity of sample B compared to that of undoped $\text{In}_{1.6}\text{Sn}_{0.2}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (Table 1, A) would change by approximately 5% (from approximately 550 to 510 S/cm) and not 73% as shown in Figure 2.

Several defect models can explain the incorporation of such large amounts of zinc while maintaining n-type conductivity (Table 2). In the first model, it is assumed that oxygen vacancies, $\text{V}_\text{O}^\bullet$, compensate for any acceptors donated by the zinc that has substituted for indium, Zn_In' . With the use of the Kroger–Vink notation, the electroneutrality condition for this compensation would be $[\text{Zn}_\text{In}'] = 2[\text{V}_\text{O}^\bullet]$. In this Discussion, $[\text{Zn}]$ refers to the concentration of excess zinc and not the total amount present in the material.

If it is assumed that the electron carrier concentration is attributed solely to anion vacancies, then it is possible to estimate the number of doping vacancies per unit formula. Assuming that each oxygen vacancy donates two electrons to the conduction band, this can be estimated by using the formula

$$\text{O vacancy} = \frac{V \times n}{(2 \text{ electrons donated/vacancy}) \times Z} \quad (1)$$

where V is the volume of the unit cell (cm^3) determined from powder XRD by pattern matching, n is the carrier concentration (electrons/ cm^3) at room temperature from Hall measurements, and Z is the number of In_2O_3 formula units per unit cell ($Z = 16$). If n is ap-

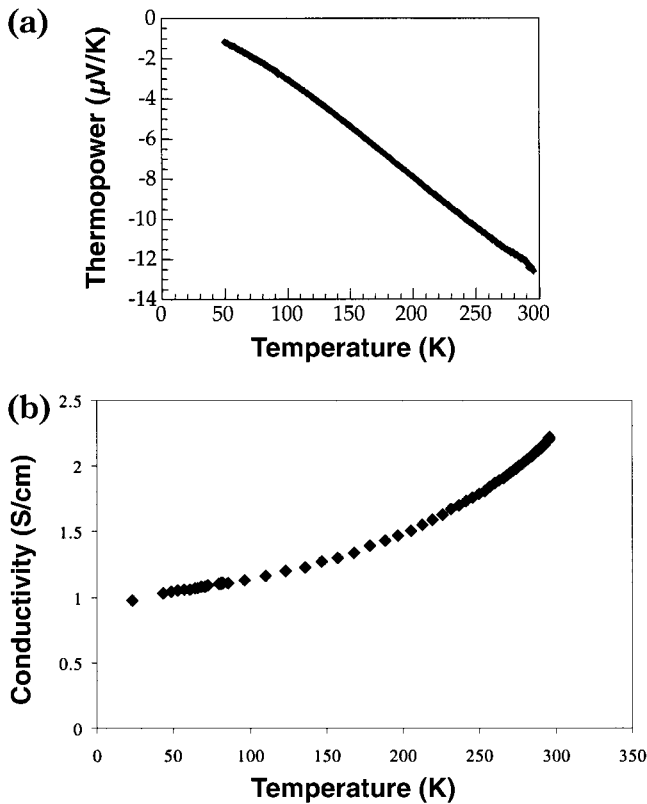


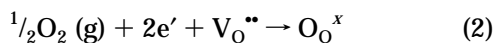
Figure 7. (a) Thermopower vs temperature for $\text{In}_{1.68}\text{Sn}_{0.12}\text{Zn}_{0.2}\text{O}_{3-\delta}$ annealed under 2 GPa of pressure. (b) Conductivity vs temperature for $\text{In}_{1.68}\text{Sn}_{0.12}\text{Zn}_{0.2}\text{O}_{3-\delta}$ annealed under 2 GPa of pressure.

Table 2. Possible Defect Chemistry in Zn-Doped $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$

explanation	electroneutrality condition
compensating oxygen vacancies	$[\text{Zn}_{\text{In}}'] = 2[\text{V}_{\text{O}}'']$
neutral zinc–oxygen vacancy complexes	$(2\text{Zn}_{\text{In}}'\text{V}_{\text{O}}'')^x$
tin nonstoichiometry	$[\text{Sn}_{\text{In}}'] \geq [\text{Zn}_{\text{In}}']$

proximately 1×10^{20} electrons/cm³ (Figure 1, C) before annealing and approximately 2×10^{18} electrons/cm³ after annealing, then the number of vacancies contributing carriers in $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$ drops from 3.24×10^{-3} to 6.38×10^{-5} per formula unit, respectively.

The number of oxygen vacancies necessary to compensate for the addition of 2% excess Zn^{2+} is calculated to be 0.02 mol per formula unit. In undoped $\text{In}_2\text{O}_{3-\delta}$, the maximum value of δ is generally 0.01.⁶ Also, according to the electroneutrality condition stated above, $[\text{V}_{\text{O}}'']$ should be mostly fixed by the concentration of excess zinc. Thus, the oxygen partial pressure, $p\text{O}_2$, should not have a large effect on $[\text{V}_{\text{O}}'']$. If the mass action law for the filling of oxygen vacancies were written as

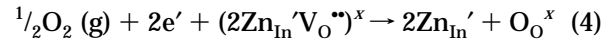


$$K_{\text{ox}} = 1/[\text{V}_{\text{O}}'']n^2p\text{O}_2^{1/2} \quad (3)$$

then the dependence of carrier concentration on $p\text{O}_2$ at constant $[\text{Zn}_{\text{In}}']$ can be calculated as $n \propto p\text{O}_2^{-1/4}$. However, when comparing as-fired and oxidized $\text{In}_{1.64}\text{Sn}_{0.16}\text{Zn}_{0.2}\text{O}_{3-\delta}$, a carrier concentration dependence of $p\text{O}_2^{-1}$ is observed (Figure 6). In addition, from the same mass action law, a dependence of the carrier

concentration on $[\text{Zn}_{\text{In}}']$ at constant $p\text{O}_2$ is calculated to be $n \propto [\text{Zn}_{\text{In}}']^{-1/2}$, yet less than an order of magnitude change in carrier concentration is observed upon doping a cosubstituted sample with up to 4% Zn.

Given the above evidence, it is likely that the incorporated zinc is not donating carriers with 100% efficiency. The most plausible reason for this is the formation of neutral $\text{Zn}-\text{V}_{\text{O}}''$ complexes, for example, $(2\text{Zn}_{\text{In}}'\text{V}_{\text{O}}'')^x$ (Table 2). Such complexes would be analogous with (but opposite to) the neutral tin–oxygen complexes that are known to form in ITO. Upon oxidation, some of these complexes may be dissociated, allowing zinc to donate an acceptor



$$K_{\text{ox}} = [\text{Zn}_{\text{In}}']^2/p\text{O}_2^{1/2}n^2[(2\text{Zn}_{\text{In}}'\text{V}_{\text{O}}'')^x] \quad (5)$$

If it is assumed that $K_{\text{ox}} \ll 1$, few neutral complexes are dissociated, even under oxidizing conditions. Thus, a large amount of zinc can be substituted into the solid solution, yet the material remains n-type.

The above defect model can also explain the mobility behavior of the as-fired vs the oxidized materials. In ITO, ionized impurities are the dominant scattering centers.^{25,26} As the material is oxidized, neutral $\text{Zn}-\text{V}_{\text{O}}''$ complexes dissociate into ionized donors (Zn_{In}'). With the increase in ionized scattering centers, there should be a decrease in carrier mobility, which is observed in Figure 6.

In addition to limited dissociation of the neutral complexes, oxidation may serve to fill any isolated oxygen vacancies inherent in the lattice of the parent structure, $\text{In}_2\text{O}_{3-\delta}$, as described in Table 2 (explanation 1). In other words, the parent structure can be thought of as $\text{In}_{2-x-y}\text{Sn}_x\text{Zn}_y\text{O}_{3-\delta-\delta'}$, where δ represents the isolated oxygen vacancies inherent in the bixbyite structure each of which donate carriers, $[\text{V}_{\text{O}}'']$, and δ' represents the oxygen vacancies associated with the neutral Zn complexes $(2\text{Zn}_{\text{In}}'\text{V}_{\text{O}}'')^x$. When the material is oxidized under high oxygen pressure, the isolated vacancies may be filled preferentially over the dissociation of the neutral complexes. This would help to explain the large decrease in electron carriers upon high-pressure oxidation.

The last possible explanation listed in Table 2 suggests that ionized Sn dopants $[\text{Sn}_{\text{In}}']$, in addition to oxygen vacancies, may be a source of electron carriers, if $[\text{Sn}_{\text{In}}'] > [\text{Zn}_{\text{In}}']$. This type of cation nonstoichiometry is seen in the analogous $\text{CdO}-\text{In}_2\text{O}_3-\text{SnO}_2$ cosubstituted bixbyite solid solution.²⁷ Less than 1% of the tin cations need to become ionized in the solid solution $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$ (assuming no holes are present) to produce carrier concentrations on the order of $n = 1 \times 10^{20}$ cm⁻³. If $K_{\text{ox}} \ll 1$, $[\text{Sn}_{\text{In}}']$ would not need to be much larger than 1% to produce n-type conductivity in the Zn-doped samples.

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Recently, several theoretical and experimental papers have been published in which p-type ZnO TCO thin films prepared by the "codoping" method are discussed.²⁸⁻³⁰ The authors reported obtaining p-type conductivity by simultaneously doping ZnO with N for O and Ga for Zn, creating acceptor-donor complexes that are thought to stabilize the material and allow for an extended solubility of the p-type dopant. Although reproduction of these results by other laboratories has not yet been successful,³¹ these findings may represent a new step in the synthesis of p-type TCOs via a codoping method.

Conclusions

It is possible to dope up to 4% of excess Zn^{2+} into cosubstituted $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$ ($x = 0.2$) while retaining the cubic bixbyite structure. The material displays overall n-type behavior, owing to the likely formation of neutral $\text{Zn}-\text{V}_\text{O}$ complexes as well as the presence of

oxygen vacancies which ionically compensate for the presence of the excess Zn^{2+} . However, a decrease in electron carrier concentration is observed with increasing incorporation of Zn^{2+} into the material. Annealing under high oxygen pressure causes a decrease in conductivity and carrier concentration. Annealing the material under physical pressures as high as 2 GPa further depresses the n-type conductivity of the material. These results imply that p-type conductivity may result if sufficient oxygen is incorporated in the bixbyite structure. Given the apparent success of p-type ZnO films obtained by codoping, it would be worthwhile to investigate the properties of Zn-doped $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-\delta}$ materials in thin film form, which may allow for a higher degree of codoping as well as facilitate the dissociation of the neutral $\text{Zn}-\text{V}_\text{O}$ complexes and the filling of oxygen vacancies.

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