

NOVEL COMPOUND AND SOLID-SOLUTION TRANSPARENT CONDUCTING OXIDES FOR PHOTOVOLTAICS

D. R. Kammler,* D. D. Edwards,* ‡ B. J. Ingram,* T. O. Mason,* G. B. Palmert†,
A. Ambrosini,† and K. R. Poeppelmeier†
Materials Research Center
Northwestern University
Evanston, IL 60208, USA

*Department of Materials Science and Engineering

†Department of Chemistry

‡Current address: Department of Ceramic Engineering and Materials Science, New York
State College of Ceramics at Alfred University, Alfred, NY 14802, USA

ABSTRACT

Future generations of photovoltaics will require transparent electrodes with enhanced conductivity while retaining optical transparency. Novel compound and solid-solution transparent conducting oxides (TCOs) have been found in the bounding binaries and ternaries of the $\text{In}_2\text{O}_3\text{-ZnO-SnO}_2\text{-Ga}_2\text{O}_3$ and $\text{In}_2\text{O}_3\text{-ZnO-SnO}_2\text{-CdO}$ quaternary systems. This work reports the subsolidus phase relations, the phase/compound solubility ranges, and the corresponding transparent conductor properties (electrical and optical) of some new TCO materials. These results suggest that phase space in these quaternaries offer rich opportunities for photovoltaic TCO development, based upon solid solution, layered compound, multi-site doping, and hybridization strategies. Preliminary work on phase relationships and TCO properties in the newly reported p-type TCO system, Cu-Al-O, are also discussed.

INTRODUCTION

Future generations of photovoltaics will require transparent electrode materials with lower sheet resistivities (to reduce losses) while maintaining optical transparency. They must also be readily processable as films in combination with other photovoltaic materials. Present electrode materials, so-called transparent conducting oxides or TCOs, possess sheet resistances on the order of $10 \Omega/\square$ transparencies greater than 80% between 350 and 900 nm, and low-surface roughness [1]. An order of magnitude improvement in conductivity from the mid- 10^3 S/cm range characteristic of the best TCO materials, e.g., indium-tin oxide (ITO) [2], would result in ease of processing (thinner films) and improvement in device performance [3].

A unique band structure is required for a material to be both conducting and transparent to visible radiation. Fan *et al.* [4] have described the band structure for ITO. An isolated conduction band exists within the base or parent oxide material, In_2O_3 , which is populated with carriers via aliovalent doping (Sn^{4+} or oxygen vacancies). The band structure of the parent oxide prevents band-to-band transitions in the visible energy spectrum that would absorb radiation, while the carriers contributed to the conduction band by the donors allow charge to be transported through the material. Such behavior appears to be limited to oxides involving late 4th and 5th row d^{10} cations (e.g., Zn, Ga, Cd, In, and Sn).

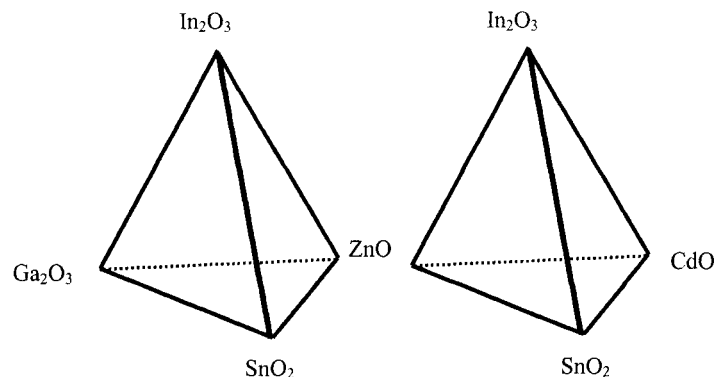


Figure 1. TCO phase space

With few exceptions, most known TCOs have been reported in the quaternary systems $\text{In}_2\text{O}_3\text{-ZnO-SnO}_2\text{-Ga}_2\text{O}_3$ and $\text{In}_2\text{O}_3\text{-ZnO-SnO}_2\text{-CdO}$ shown in Figure 1. Three of the vertices, i.e., In_2O_3 , ZnO and SnO_2 , are well-known TCO hosts capable of being doped to induce TCO behavior. However, given the extensive research on these materials over the past few decades, it seems unlikely that TCOs with enhanced behavior will be developed based upon such “single-cation” materials. During the 1990s, there have been a number of reports of binary and ternary compositions in the two quaternaries of Figure 1 that exhibit promising TCO behavior in thin-films. The present study is devoted to complex, multiple TCO-cation oxides, and the systematic investigation of phase space (“guided” combinatoric chemistry) of these important systems for novel TCO phases/compounds.

While thin-films often exhibit different structural, electrical, and optical properties from their bulk counterparts, an understanding of the bulk phases and their equilibrium phase relationships is nevertheless important for interpreting the processing, phase behavior, and TCO properties of thin-films. The bulk phase relationships are certainly applicable to the manufacture of sputtering targets used in sputter-deposition of TCO films. Finally, an understanding of the bulk crystal structures, including coordination environments, multiple cation sites, and 2D layering, together with the solubility limits, help us to develop and refine our strategies for engineering phases with enhanced TCO properties.

EXPERIMENTAL PROCEDURE

Samples were prepared from In_2O_3 , ZnO , Ga_2O_3 , SnO_2 , and CdO powders (>99.9% purity on a cation basis, Aldrich Chemical Company, Inc). Pre-weighed amounts of powders were ground under acetone in an agate mortar and pestle. Disk-shaped pellets were pressed in cylindrical dies and fired in alumina crucibles surrounded by beds of their constituent powders, to minimize contamination from the crucible and limit volatilization of the constituent oxides. Samples containing CdO were fired inside a

cylindrical alumina crucible enclosed in a long alumina tube sealed at the opposite end to further control volatilization. Samples were fired in air at 1100°C for several days, reground and re-pelletized, fired a second time at 1250°C for several more days, and finally quenched in air. Samples containing CdO had to be initially fired at 1000°C for one day, re-pelletized, and then fired at 1175°C for a second day in order to minimize volatilization of CdO. Phase composition was determined via X-ray powder diffraction (Scintag, U.S.A & Rigaku, Japan) using Cu-K α radiation.

Room temperature 4-pt. conductivity was measured using a linear 4-pt. probe. The effects of finite thickness and diameter on conductivity were corrected using the method described by Smits [5]. Furthermore, the measurements were corrected for the presence of porosity; conductivity was divided by the specimen's percent theoretical density in most cases or the symmetric medium equation of McLachlan [6] was employed along the Cd₂SnO₄ – CdIn₂O₄ binary.

Diffuse reflectance was measured from 200 to 900 nm using a double-beam spectrophotometer with an integrating sphere. Baseline spectra were collected with pressed polytetrafluoroethylene (PTFE) powder compacts placed in the sample and reference beams. Diffuse reflectance measurements on bulk samples are analogous to transmission measurements on thin-films [7].

DISCUSSION AND RESULTS

The In₂O₃-ZnO-Ga₂O₃ Ternary

The In₂O₃-ZnO binary has been the subject numerous investigations for TCO films. Wang *et al.* reported a conductivity of 1100 S/cm for sputtered ZnO films containing less than 5-atomic percent indium [8]. Minami *et al.* reported a conductivity of 2900 S/cm for Zn₂In₂O₅ films sputtered from polycrystalline targets containing 10-60-atomic percent zinc [9,10].

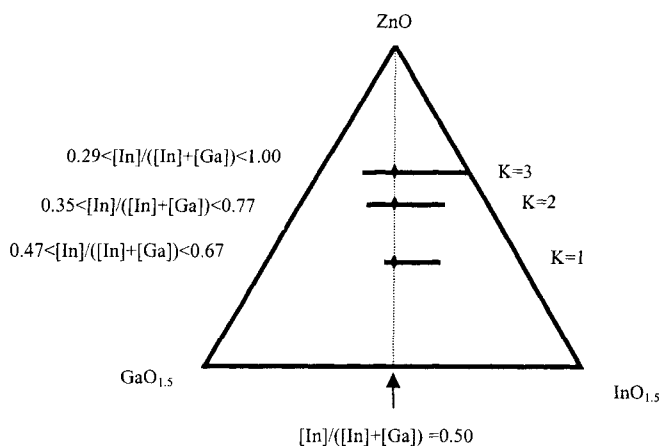


Figure 2. Psuedo InO_{1.5}-ZnO-GaO_{1.5} ternary showing extent of the solutions In_{1-x}Ga_{1+x}O₃(ZnO)_k (k=1,2, and 3)

We reported bulk phase relations in the $\text{In}_2\text{O}_3\text{-ZnO}$ system that consists of a series of intergrowth compounds, $\text{In}_2\text{O}_3(\text{ZnO})_k$ ($k=3,4,5,7,11$) [11]. Kasper managed to synthesize the $k=2$ member of the series, but was unable to produce the $k=1$ member of the solution [12]. Nakumura *et al.* [13] succeeded in producing an isostructural solid solution, $\text{In}_{1-x}\text{Ga}_{1+x}\text{O}_3(\text{ZnO})_k$, for the $k=1$ member of the family in addition to $\text{In}_{1-x}\text{Ga}_{1+x}\text{O}_3(\text{ZnO})_k$ ($k=2-9, 11, \text{ and } 13$). These compounds are believed to consist of equal numbers of InO_2^- and $(\text{GaZn}_k)\text{O}_{k+1}^+$ layers. It is thought that the In^{+3} cation is octahedrally coordinated within InO_2^- layers while M^{+3} and Zn^{+2} occupy distorted trigonal-bipyramidal and tetrahedral sites within the $(\text{MZn}_k)\text{O}_{k+1}^+$ layers [13]. The solubility limits for the $k=1, 2$ and 3 intergrowths were determined as indicated in Figure 2, and their electrical conductivity and absorption edges (by diffuse reflectance) were determined as a function of the $[\text{In}]/([\text{In}]+[\text{Ga}])$ ratio [14].

The absorption edge increases with increasing k and with increasing $[\text{In}]/([\text{In}]+[\text{Ga}])$ ratio. The minimum absorption edge of 325 nm was measured for the as-fired $k=2$ sample $\text{In}_{0.7}\text{Ga}_{1.3}\text{O}_3(\text{ZnO})_2$. An as-fired $k=3$ member, $\text{In}_{0.6}\text{Ga}_{1.4}\text{O}_3(\text{ZnO})_3$, has an absorption edge of 330 nm. Electrical conductivity increases with decreasing k and with an increasing ratio of $[\text{In}]/([\text{In}]+[\text{Ga}])$. While the maximum conductivity of 250 S/cm was obtained for the reduced $k=3$ sample with zero Ga content (i.e., $\text{In}_2\text{O}_3(\text{ZnO})_3$), the data indicated that the $k=2$ intergrowth should have a higher conductivity if it can be stabilized out to the $\text{In}_2\text{O}_3\text{-ZnO}$ binary line. The trend of increasing conductivity with decreasing k implies that conduction is taking place along the octahedral InO_2^- layers in these intergrowth compounds [14].

The $\text{In}_2\text{O}_3\text{-ZnO-SnO}_2$ Ternary

Phillips *et al.* found high conductivity in bulk $\text{Zn}_3\text{In}_2\text{O}_6$ doped with Sn and reported a new TCO of composition $\text{ZnIn}_{1.7}\text{Sn}_{0.3}\text{O}_{4.15}$ within the $\text{In}_2\text{O}_3\text{-ZnO-SnO}_2$ ternary [15]. Along the ZnO-SnO_2 binary, Zn_2SnO_4 and ZnSnO_3 have been reported as TCO films [16,17].

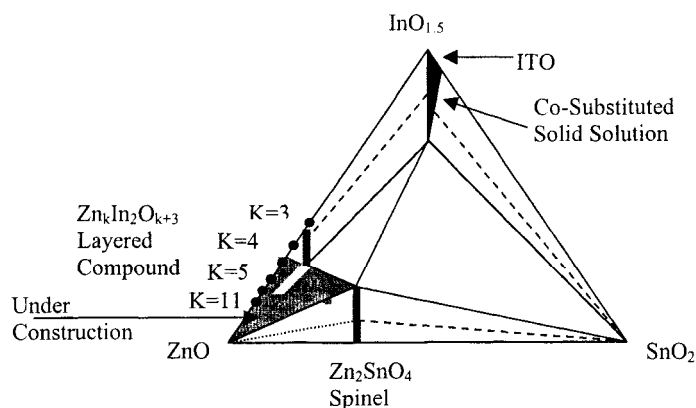


Figure 3. Bulk Phase Relations for system $\text{InO}_{1.5}\text{-SnO}_2\text{-ZnO}$ at 1250°C

The bulk phase relations for the In_2O_3 - SnO_2 - ZnO system appear in Figure 3. There is a large ternary spinel solution, $\text{Zn}_{2-x}\text{Sn}_{1-x}\text{In}_{2x}\text{O}_{4-8}$ ($x=0$ to 0.45) and a ternary Zn, Sn co-substituted form of ITO with the formula, $\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_{3-6}$ ($x=0$ to 0.4) [18,19]. The conductivity of reduced specimens along the spinel solution increases with increasing x to reach a maximum of 3 S/cm at the terminal point. Band gap decreases with x from a high of 3.6 eV for Zn_2SnO_4 to a low of 3.4 eV for the terminal point [18]. Thus, although specimens along this line show TCO properties, the best conductivity is a factor of 1000 lower than ITO. Reduced specimens in the co-substituted ITO solution at the top of Figure 3 show promise for TCO applications. Specimen conductivity decreases with x from a high of 2600 S/cm at $x = .05$ to a low of 800 S/cm at the terminal point of the solution. Band gap decreases with increasing x as well from a high of 3.5 eV at $x = 0.05$ to a low of 2.9 eV at the terminal point of the solution [19].

The In_2O_3 - SnO_2 - Ga_2O_3 Ternary

As in the above ternary systems, numerous thin-film reports have also originated out of the In_2O_3 - SnO_2 - Ga_2O_3 system. TCO films of composition $\text{GaIn}_{1-x}\text{Sn}_x\text{O}_3$ ($0 < x < 0.2$) having the β - Ga_2O_3 crystal structure, conductivity as high as 365 S/cm, and optical properties better than ITO have been reported [20,21]. $\text{Ga}_{2-x}\text{In}_x\text{O}_3$ films have been reported having a conductivity of 360 S/cm for $x=1$ [22]. Shannon and Prewitt [23] have reported $\text{Ga}_{2-x}\text{In}_x\text{O}_3$ ($0 < x < 1$) having the β - Ga_2O_3 structure as well as a high pressure hexagonal form of GaInO_3 . The bulk phase relations in this system at 1250°C were established as shown in Figure 4 [24]. We observed a solid solution, $\text{Ga}_{2-x}\text{In}_x\text{O}_3$, for $0 < x < 0.882$ at 1000°C and $0 < x < 0.828$ at 1400°C , with no evidence of a stable GaInO_3 ($x=1$) compound [25]. Several new ternary phases were discovered within this system as can be seen in Figure 4. The M-phases shown on the left of the diagram are intergrowths of the β - Ga_2O_3 structure and the rutile structure of SnO_2 [24]. These phases exhibit conductivities smaller than 10^{-2} S/cm and optical band gaps of ~ 4 eV. The T-phase on the lower-right portion of the diagram exhibits conductivities of 300-500 S/cm after reduction in forming gas and band gaps of ~ 3 eV.

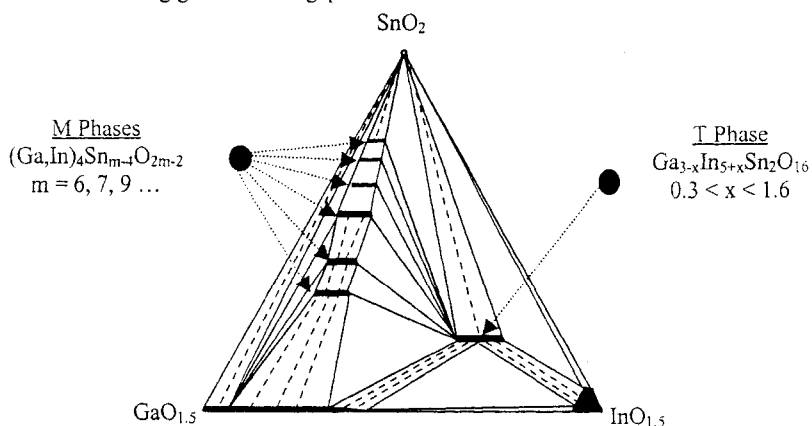


Fig. 4 Bulk phase relations in the system $\text{InO}_{1.5}$ - $\text{GaO}_{1.5}$ - SnO_2

Like ITO, the T-phase is an anion-deficient fluorite-derivative, however, it is missing one of the distorted InO_6 octahedra present in the ITO structure [26]. The absence of this “dopant” site, where Sn^{+4} could substitute for In^{+3} , may explain why the conductivity of the T-phase is much lower than that of ITO [26]. In contrast, the high conductivity of the (Sn,Zn) co-substituted ITO in Figure 3 could be attributed to the presence of this site, as this phase is isostructural with ITO. In light of the phase relations shown in Figure 4, we believe the high conductivity reported for $\text{GaIn}_{1-x}\text{Sn}_x\text{O}_3$ ($0 < x < 0.2$) films can be attributed to the presence of the T-phase.

The In_2O_3 - SnO_2 -CdO Ternary

In addition to ITO, several other TCOs have been reported in the In_2O_3 - SnO_2 -CdO system. Nozik [27] reported that powders of orthorhombic Cd_2SnO_4 have conductivities as high as 10 S/cm, and amorphous TCO films have conductivities up to 1330 S/cm (with mobilities as high as $100 \text{ cm}^2/\text{Vs}$) and band gaps as high as 2.85 eV. Low-temperature synthesis of bulk Cd_2SnO_4 has been reported to yield a spinel phase [27,28]. Bulk Cd_2SnO_4 has also been prepared in spinel form at high temperatures and pressures [29]. Cd_2SnO_4 has been prepared in thin-film form with a spinel structure with conductivities as high as 6700 S/cm [30] and 8300 S/cm [31]. Shannon *et al.* reported the single crystal CdSnO_3 in both illmenite ($\sigma=10^{-5}$ S/cm) and distorted perovskite forms ($\sigma=1000$ S/cm), plus orthorhombic Cd_2SnO_4 ($\sigma=10^{-3}$ S/cm) and CdIn_2O_4 in spinel form ($\sigma=2000$ S/cm) [32]. Little is known about the interior of this ternary system. Shannon *et al.* [32] have prepared single crystal $\text{CdIn}_{2-x}\text{Sn}_x\text{O}_4$ ($\sigma=450$ S/cm) from a flux of 2.5 CdO: 1.0SnO₂: 0.5 In₂O₃. Cardile [33] attempted to dope Cd_2SnO_4 with *In* but reported negligible increase in conductivity.

Preliminary bulk phase relations for the In_2O_3 - SnO_2 -CdO system appear in Figure 5. A large spinel solution $\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$ exists over the range $0 < x < 0.75 \pm 0.05$.

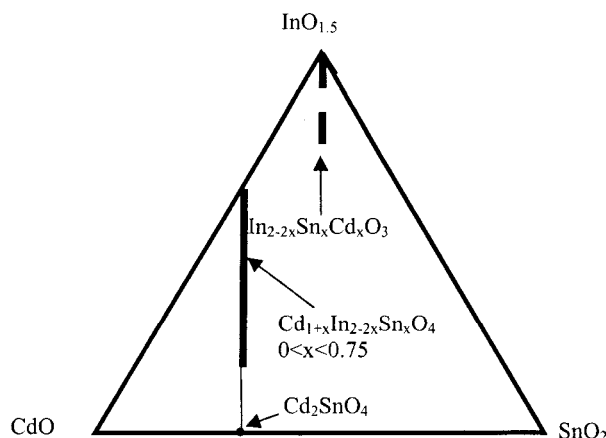


Figure 5. Preliminary bulk phase relations for the system $\text{InO}_{1.5}$ - SnO_2 -CdO

Specimens with compositions $0.75 < x < 1.0$ were biphasic and consisted of the terminal spinel composition, $\text{Cd}_{1.75}\text{In}_{0.5}\text{Sn}_{0.75}\text{O}_4$, and orthorhombic Cd_2SnO_4 , which appears to be a line compound. Conductivity increases with x from 1600 S/cm at $x=0$ to 2600 S/cm at $x=0.76$. (Note: This sample had a small amount of the orthorhombic Cd_2SnO_4 phase present). Extrapolating the conductivity vs. x to $x=1$ from the spinel solution yields a value near 3000 S/cm. This seems consistent with the fact that high conductivity Cd_2SnO_4 thin-films possess the spinel structure [30,31]. Cardile *et al.* [34] noted a strong correlation between the Sn s-electron density and conductance in cadmium stannate films using ^{119}Sn Mössbauer spectroscopy. The increase in conductivity with x measured for the $\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$ solution could be indicative of a similar increase in Sn s-electron density with x .

Band gaps determined from diffuse reflectance decreased with x from a value of 3.0 eV at $x=0$ to 2.7 eV at $x=0.76$. Both conductivity and band gap show an inflection point near the middle of the solution. This could be indicative of cation ordering. ^{119}Sn Mössbauer spectroscopy studies on Cd_2SnO_4 [34,35] indicate that Sn^{+4} is octahedrally coordinated and therefore Cd_2SnO_4 should have an inverse distribution of cations. Both Skribljak *et al.* [36] and Rasines [37] determined via XRD that CdIn_2O_4 has an inverse cation distribution while Shannon *et al.* [32] determined via XRD that CdIn_2O_4 is a normal spinel. Given that both In^{+3} and Cd^{+2} are strong tetrahedral-preferring cations (38) and have identical scattering factors [39], it seems that a technique such as neutron diffraction is better suited to resolve the site distribution in CdIn_2O_4 .

The top of Figure 5 shows the presence of a solid solution, $\text{In}_{2-2x}\text{Sn}_x\text{Cd}_x\text{O}_4$, which is presently under investigation. Several single-phase specimens have already been prepared along this solution line and were found to possess the cubic bixbyite structure of In_2O_3 . If an extensive Cd,Sn co-substituted In_2O_3 solid solution exists, in analogy to that in the In_2O_3 -ZnO-SnO₂ system, its TCO properties could be of considerable interest.

The CuO-Al₂O₃ Binary

All the TCOs within the phase space shown in Figure 1 are n-type. The possibility of a p-type TCO is interesting from a device standpoint. The report of p-type conduction in the CuO-Al₂O₃ system raised the possibility of making a transparent transistor. Kawazoe, *et al.* reported p-type conduction in CuAlO_2 thin-films with a conductivity of 1 S/cm, a mobility of 10.4 cm²/V-s, an absorption edge of 350 nm, and transmittance as high as 55% in the visible region [40]. Previously, Benko *et al.* [41] prepared CuAlO_2 in bulk form with a measured conductivity of 1.7×10^{-3} S/cm, a thermoelectric power of 670 $\mu\text{V}/\text{K}$ indicating p-type conduction, a mobility less than 10^{-1} cm²/Vs, and multiple transitions between 1.65 and 3.5 eV. Such a low mobility led them to hypothesize that CuAlO_2 is a small polaron conductor [41]. Our preliminary studies of the bulk phases and phase relationships in the Cu-Al-O system have revealed that: 1) CuAlO_2 is a "line" compound, 2) it is quite difficult to dope, 3) conductivity is quite low ($< 10^3$ S/cm), and 4) carrier concentration, although p-type in character, is quite low (based upon high thermopower values).

Summary of Electrical and optical properties

Table I summarizes our 4pt. conductivity and band gap (by diffuse reflectance) values determined for bulk polycrystalline TCO materials found to date in the quaternary systems shown in Figure 1 and in the CuO-Al₂O₃ system. It should be stressed that these

bulk materials are randomly oriented polycrystalline specimens with high porosities. Oriented films made of these materials generally show much higher conductivities.

Table 1. Electrical and Optical Results for Novel TCO Phases and Solid Solutions

<u>TCO Phase</u>	<u>*4pt. Conductivity(S/cm)</u>	<u>*Optical Band gap (eV)</u>
$\text{In}_{1-x}\text{Ga}_{1+x}\text{O}_3(\text{ZnO})_k$	0.15-250	2.9-3.8
$\text{Zn}_{2-x}\text{Sn}_{1-x}\text{In}_2\text{O}_4$	0-3	3.2-3.6
$\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_3$	800-2600	2.9-3.5
$\text{Ga}_{4-4x}\text{In}_{4x}\text{Sn}_m\text{O}_{6+2m}$	$<10^{-2}$	4.0
$\text{Ga}_{3-x}\text{In}_{5+x}\text{Sn}_2\text{O}_{16}$	300-500	3.0
$\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$	1600-2600	2.7-3.1
CuAlO_2	10^{-3}	-----

* All specimens reduced except $\text{Cd}_{1+x}\text{In}_{2-2x}\text{Sn}_x\text{O}_4$, which is as-fired. Band gaps for $\text{In}_{1-x}\text{Ga}_{1+x}\text{O}_3(\text{ZnO})_k$ are for as-fired samples.

CONCLUSIONS

We have determined bulk phase relations for several bounding ternaries of the In_2O_3 - Ga_2O_3 - ZnO - SnO_2 and the In_2O_3 - ZnO - SnO_2 - CdO TCO quaternary systems. These ternary diagrams show the existence of a number new TCO phases and extensive solid solutions of pre-existing TCO phases. A number of important observations emerge that may present useful strategies for the development of novel TCOs with enhanced properties. First, isovalent co-substitution (e.g., Zn^{2+} and Sn^{4+} for two In^{3+} in In_2O_3) may be a means to alter (enhance?) the properties of existing TCO host materials. We are currently investigating this possibility in Cd,Sn co-substituted In_2O_3 . Second, 2D-layered compounds, e.g., the $\text{In}_2\text{O}_3(\text{ZnO})_k$ materials, provide an opportunity to preferentially dope "spacer" layers for carrier injection into the conducting layers that are otherwise unperturbed. We are currently investigating this as a means of developing enhanced-mobility TCO phases. Electronic hybridization involving two or more TCO-active species is yet another means of achieving high-mobility TCOs. We believe this to be the case in the spinel phase of Cd_2SnO_4 , although further experimental and theoretical studies are required to confirm the origin of the reported high mobility in this important new material. Finally, there is the potential to discover novel ternary and higher compounds with outstanding TCO properties. The T-phase in the In_2O_3 - SnO_2 - Ga_2O_3 system is an excellent example of a previously unknown chemistry and crystal structure that has produced a novel TCO material. This suggests that novel compound and solid-solution phases remain to be discovered in the phase space outlined in Figure 1.

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