

A new transparent conducting oxide in the $\text{Ga}_2\text{O}_3\text{--In}_2\text{O}_3\text{--SnO}_2$ system

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A new transparent conducting oxide (TCO), which can be expressed as $\text{Ga}_{3-x}\text{In}_{5+x}\text{Sn}_2\text{O}_{16}$; $0.2 \leq x \leq 1.6$, has been identified. The equilibrium phase relationships of this new material with respect to three other TCOs in $\text{Ga}_2\text{O}_3\text{--In}_2\text{O}_3\text{--SnO}_2$ are reported. The optical properties of this phase are slightly superior to Sn-doped indium oxide (ITO) and depend on composition. A room-temperature conductivity of $375 \Omega \text{ cm}^{-1}$ was obtained for H_2 -reduced $\text{Ga}_{2.4}\text{In}_{5.6}\text{Sn}_2\text{O}_{16}$. This value is an order of magnitude lower than commercial ITO films, but comparable to values reported for bulk, polycrystalline Sn-doped In_2O_3 . © 1997 American Institute of Physics. [S0003-6951(97)03513-4]

Transparent conducting oxides (TCOs) are used in a variety of applications including flat panel displays and solar energy conversion devices. Three structurally distinct TCOs have been reported in the $\text{Ga}_2\text{O}_3\text{--In}_2\text{O}_3\text{--SnO}_2$ system. Both tin oxide, which crystallizes in the tetragonal rutile structure, and tin-doped indium oxide (ITO), which crystallizes in the cubic bixbyite structure, are currently used for commercial applications.¹ Experimental TCOs prepared as $\text{GaIn}_{1-x}\text{Sn}_x\text{O}_3$ with $x=0\text{--}0.2$ are reported to crystallize in the monoclinic β -gallia crystal structure. The β -gallia-based TCOs exhibit superior transparency in the green-blue region in comparison to ITO, but the highest conductivities reported for thin films are on the order of $350 \Omega \text{ cm}^{-1}$ which is approximately ten times lower than that observed in commercial ITO.^{2,3}

In this letter, we report the synthesis and characterization of yet another TCO in the $\text{Ga}_2\text{O}_3\text{--In}_2\text{O}_3\text{--SnO}_2$ system and report its phase relationships with other TCO phases in the system. The new material, which can be expressed as $\text{Ga}_{3-x}\text{In}_{5+x}\text{Sn}_2\text{O}_{16}$; $0.2 \leq x \leq 1.6$, crystallizes in a tetragonal structure that, like the bixbyite structure of In_2O_3 , can be derived from a cubic-fluorite parent structure.⁴ Annealing the polycrystalline, bulk ceramics in a reducing atmosphere results in a room-temperature conductivity ($\sigma=375 \Omega \text{ cm}^{-1}$) comparable to that reported for the β -gallia-based TCOs but approximately ten times lower than commercial ITO films. Optical properties determined by diffuse reflectance spectroscopy are slightly superior to those of polycrystalline ITO (3% Sn) and improve with increasing Ga content.

A series of compositions were prepared from commercially obtained (>99.99% pure) In_2O_3 , Ga_2O_3 , and SnO_2 powders. Weighed amounts of the dried starting powders were moistened with acetone and ground together with a mortar and pestle. Pellets pressed from the dried powders were heated in high-density alumina crucibles at 1250°C for at least 72 h and subsequently quenched in air. To prevent contamination from the alumina crucibles, the pellets were placed upon a powder bed of the same composition during firing. Weight loss during firing was typically less than 1%. The phase composition of the samples was determined by x-ray diffraction (Scintag, USA). The densities of phase-pure

pellets were 60%–65% of theoretical. The diffuse reflectance spectra of selected as-fired samples were measured from 200 to 900 nm using a double-beam spectrophotometer with integrating sphere (Cary 1E with Cary 1/3 attachment, Varian, USA). A pressed polytetrafluoroethylene (PTFE) powder compact (Varian part number 04-101439-00) was used as a high transmission reference. Simultaneous four-point conductivity and thermoelectric coefficient measurements were conducted on rectangular bars (approximately $5 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$) cut from the sintered pellets using an experimental apparatus described previously.⁵ Electrical measurements were conducted from room temperature to 500°C in both oxidizing (dry air) and reducing (4% $\text{H}_2\text{--}96\% \text{N}_2$) environments.

Figure 1 shows the diffractogram of $\text{Ga}_{2.4}\text{In}_{5.6}\text{Sn}_2\text{O}_{16}$ in comparison to that of ITO (3% Sn). The diffraction patterns are similar with respect to the four most intense reflections. Yet, numerous small reflections from the new phase cannot be accommodated by a cubic structure. The new phase has a tetragonal structure in which Sn is incorporated as a structural element rather than as a substitutional dopant as it is in ITO.⁴ The cell dimensions of the new phase increase with

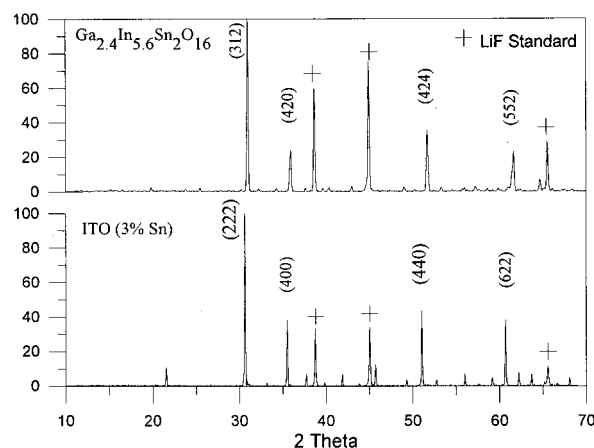


FIG. 1. Powder x-ray diffraction pattern (Cu $K\alpha$ radiation) of T -phase composition, $\text{Ga}_{2.4}\text{In}_{5.6}\text{Sn}_2\text{O}_{16}$, in comparison to ITO (3% Sn).

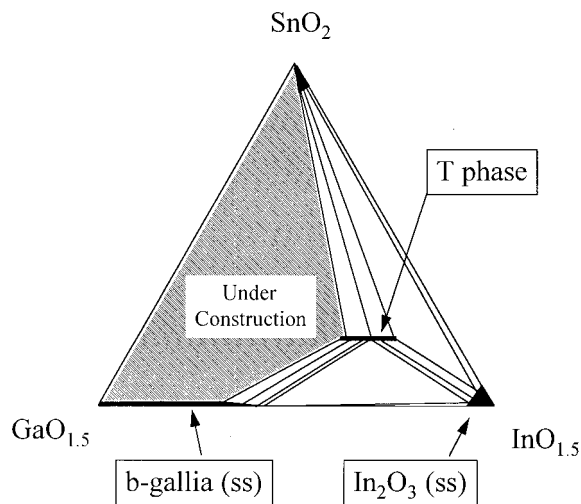


FIG. 2. Phase relationships among TCOs in the Ga₂O₃-In₂O₃-SnO₂ system.

increasing indium content with $a=11.133(2)-11.212(2)$ Å and $c=9.96(1)-10.101(1)$ Å.

Figure 2 illustrates the phase relationships of Ga_{3-x}In_{5+x}Sn₂O₁₆, identified as the *T* phase, to the other TCOs in the Ga₂O₃-In₂O₃-SnO₂ system. This diagram is a work-in-progress based on lattice-parameter measurements and electron probe microanalysis. The black-colored regions (thick lines and triangles) indicate single-phase regions. The thin, black lines indicate tie lines between two single-phase regions. Details of the region shaded in gray are not fully established, but are not particularly relevant to this discussion. Because this is a work-in-progress, some of the phase boundaries shown for the single-phase regions are tentative. Specifically, the ternary solid-solubility limits shown for the SnO₂ and In₂O₃ solid solutions are estimates based on the binary solubility limits.^{6,7} Details regarding the solubility limits of the β -gallia phase and the new *T* phase are discussed below.

The new *T* phase is shown to exist along a line at [Sn] = 0.20 (cation basis) with [In] ranging from 0.52 to 0.66 (cation basis). Because samples prepared with [Sn] = 0.19 were multiphasic and because of structural considerations,⁴ we have concluded that the lower limit of stability with respect to [Sn] is 0.20. At [Sn] < 0.20, the *T* phase coexists with either a β -gallia solid solution or an In₂O₃ solid solution or both. Although the upper limit of Sn solubility in the *T* phase has not been conclusively determined, we expect it to be quite low. For example, a sample prepared with [Sn] = 0.22 and [In] = 0.58 is multiphasic, containing a SnO₂ solid solution in addition to the *T* phase. Whether or not Sn can be incorporated as a substitutional dopant for In with 0.20 < [Sn] < 0.22 is currently under investigation. For [Sn] = 0.20 and [In] > 0.66, the *T* phase coexists with both a SnO₂ solid solution and an In₂O₃ solid solution. For [Sn] = 0.20 and [In] < 0.52, the *T* phase coexists with a β -gallia solid solution and an additional phase currently under investigation (not shown in Fig. 2).

Figure 2 also illustrates several interesting features regarding the other TCOs in the system. First, GaInO₃ does not

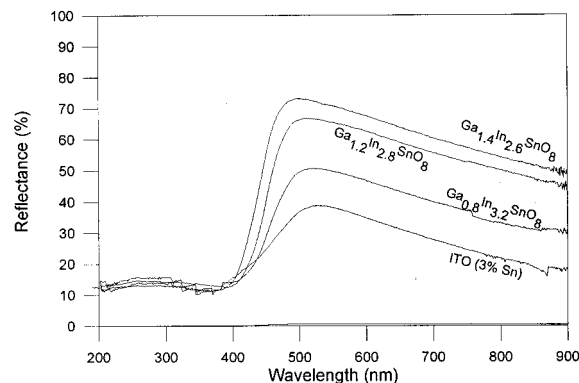


FIG. 3. Diffuse reflectance spectra of *T*-phase compositions and ITO (3% Sn).

form at 1250 °C, and is not a stable composition between 1000 and 1400 °C.⁶ At 1250 °C, the equilibrium solid-solubility limit of In₂O₃ in β gallia is 43%,⁶ not 50% as reported in the literature.⁸ Second, the solid solubility limit of Sn in the β -gallia structure is quite low in agreement with results reported by Kwo *et al.* for sputtered films.⁹ At 1250 °C, the Sn solubility in the bulk β -gallia solid solutions (Ga_{2-2x}In_{2x}O₃ with $x=0-0.43$) is less than 2%. Consequently, compositions prepared as GaIn_{1-x}Sn_xO₃ with 0.05 ≤ x ≤ 0.20 under the conditions used in this study contained the new *T* phase in addition to a β -gallia solid solution. We believe that the limited solubility of Sn in the β -gallia solid solutions as well as the phase relationships illustrated in Fig. 2 may explain the weak dependency of conductivity on [Sn] previously reported for the β -gallia-based TCOs,^{2,3,8} but we also recognize that nonequilibrium conditions often exist during the synthesis of thin-film materials.

The color of the quenched *T*-phase samples ranged from yellow-green (high gallium content) to green (low gallium content). The color of an ITO (3% Sn) sample prepared under the same conditions was also green, but darker than any of the *T*-phase compositions. Figure 3 compares the diffuse reflectance spectra of *T*-phase compositions to the spectrum of polycrystalline ITO (3% Sn). Diffuse reflectance spectra are similar to transmission spectra. The fundamental absorption edges of the *T*-phase compositions as well as the ITO is around 400 nm, suggesting a band gap near 3 eV. The transmission (reflectance) at $\lambda > 400$ nm of the *T*-phase compositions is higher than that of ITO (3% Sn) and increases with gallium concentration. This implies that the *T*-phase may have a lower absorption coefficient than ITO in this region, but also implies that the *T*-phase compositions may have a smaller carrier concentration.

Results from combined thermopower and conductivity measurements are consistent with electron doping by oxygen vacancies. The conductivity of air-quenched Ga_{2.4}In_{5.6}Sn₂O₁₆ was thermally activated ranging from approximately 2 Ω cm⁻¹ at 25 °C and 20 Ω cm⁻¹ at 500 °C. Prolonged annealing in air above 300 °C resulted in a decrease in the conductivity presumably due to filling of oxygen vacancies established at the higher processing temperature. Annealing in forming gas (4% H₂-96% N₂) at 500 °C for several hours resulted in a hundredfold increase in the

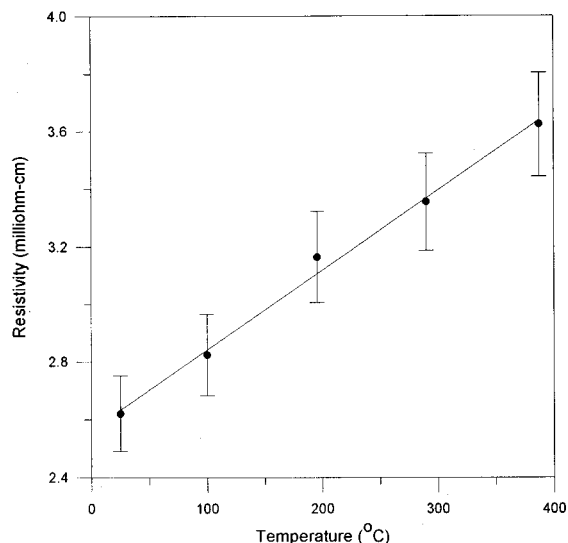


FIG. 4. Electrical resistivity of air-annealed $\text{Ga}_{2.4}\text{In}_{4.5}\text{Sn}_2\text{O}_{16}$ as a function of temperature.

room-temperature conductivity to $375 \Omega \text{ cm}^{-1}$. The highest conductivity achieved is an order of magnitude lower than commercial ITO films, but is comparable to the low-end values of conductivity reported for bulk, polycrystalline Sn-doped In_2O_3 which ranges from $550\text{--}1000 \Omega \text{ cm}^{-1}$.^{10–12} Whether or not significant increases in conductivity will be realized in dense, thin-film material is currently under study. The reduced *T*-phase sample exhibited slightly metallic behavior with a temperature coefficient of resistivity (TCR) of $2.9 \mu\Omega \text{ cm/K}$ as shown in Fig. 4. Annealing the reduced sample in air at 500°C again resulted in a decrease in conductivity and the restoration of thermally activated conduction as illustrated in Fig. 5. At 500°C , the thermoelectric coefficient ranged from $-75 \mu\text{V/K}$ in reducing conditions to $-175 \mu\text{V/K}$ in oxidizing conditions.

In summation, a new transparent conducting oxide (TCO) in the $\text{Ga}_2\text{O}_3\text{--In}_2\text{O}_3\text{--SnO}_2$ system is reported with a composition that can be expressed as $\text{Ga}_{3-x}\text{In}_{5+x}\text{Sn}_2\text{O}_{16}$; $0.2 \leq x \leq 1.6$. The new TCO exhibits optical properties that are slightly superior to ITO. In addition to improved optical properties, the new *T*-phase compositions may provide considerable economic advantage over ITO because they require less indium. The electrical conductivity of a reduced, porous *T*-phase sample was approximately ten times lower than that reported for commercial ITO films. Efforts are currently under way to prepare dense thin films and to characterize the

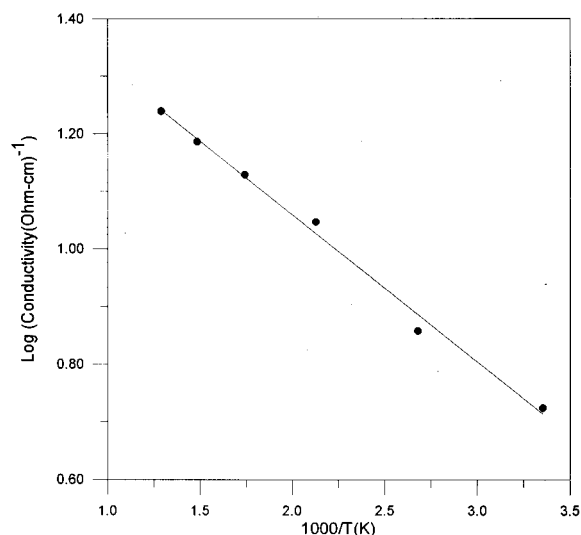


FIG. 5. Electrical conductivity of reduced $\text{Ga}_{2.4}\text{In}_{4.5}\text{Sn}_2\text{O}_{16}$ as a function of reciprocal temperature.

defect chemistry of the new phase in order to determine the extent to which the electrical and optical properties can be optimized for TCO applications.

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- ¹N. R. Lynam, Electrochemical Society Proceedings, 1990 (unpublished), Vol. 90–92, p. 201.
- ²R. J. Cava, J. M. Phillips, J. Kwo, G. A. Thomas, R. B. van Dover, S. A. Carter, J. J. Krajewski, W. F. Peck, Jr., J. H. Marshall, and D. H. Rapkine, Appl. Phys. Lett. **64**, 2071 (1994).
- ³J. M. Phillips, J. Kwo, G. A. Thomas, S. A. Carter, R. J. Cava, S. Y. Hou, J. J. Krajewski, J. H. Marshall, W. F. Peck, D. H. Rapkine, and R. B. van Dover, Appl. Phys. Lett. **65**, 115 (1994).
- ⁴D. D. Edwards, P. A. Salvador, T. O. Mason, F. Goutenoire, K. R. Poepelmeier, H. Zhang, and L. Marks (unpublished).
- ⁵A. Trestman-Matts, S. E. Dorris, and T. O. Mason, J. Am. Ceram. Soc. **66**, 589 (1983).
- ⁶D. D. Edwards, P. E. Folkens, and T. O. Mason, J. Am. Ceram. Soc. **80**, 253 (1997).
- ⁷H. Enoki, J. Echigoya, and H. Suto, J. Mater. Sci. **26**, 4110 (1991).
- ⁸R. D. Shannon and C. T. Prewitt, J. Inorg. Nucl. Chem. **30**, 1389 (1968).
- ⁹J. Kwo, S. A. Carter, R. J. Cava, S. Y. Hou, J. M. Phillips, D. H. Rapkine, G. A. Thomas, and R. B. Van Dover, Mater. Res. Soc. Symp. Proc. **345**, 241 (1994).
- ¹⁰T. Omata, N. Ueda, K. Ueda, and H. Kawazoe, Appl. Phys. Lett. **64**, 1077 (1994).
- ¹¹S. J. Wen, G. Campet, J. Portier, G. Couturier, and J. B. Goodenough, Mater. Sci. Eng. B **14**, 115 (1992).
- ¹²S. J. Wen, G. Couturier, J. P. Chaminade, E. Marquestaut, J. Claverie, and P. Hagenmuller, J. Solid State Chem. **101**, 203 (1992).