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DEFECT STRUCTURE OF INDIUM TIN OXIDE AND ITS RELATIONSHIP TO CONDUCTIVITY

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Doping In_2O_3 with tin results in an improved transparent conducting oxide (TCO). Although indium tin oxide (ITO) is the most frequently used commercial TCO, its defect structure is still uncertain. Previously, its defect chemistry has been inferred based on the conductivity of the material. To directly study the defect structure of ITO, we prepared powders under different processing environments and performed neutron powder diffraction. Structural information was obtained by performing Rietveld analysis. The results include positions of the atoms, their thermal displacements, the fractional occupancy of the defect oxygen site, and the fractional occupancies of Sn on each of the two nonequivalent cation sites, showing a strong preference for the b site. These structural results are correlated with the measured electrical properties of the same samples.

I. INTRODUCTION

Tin-doped indium oxide, also known as ITO (for indium tin oxide), is a transparent conducting oxide with a wide range of applications, including flat-panel and liquid displays, solar cells, and energy-efficient windows¹. The host lattice, In_2O_3 , crystallizes in the cubic bixbyite structure (C-type rare-earth sesquioxide structure) $Ia\bar{3}$ space group.

The bixbyite structure has 80 atoms per unit cell and is closely related to the fluorite structure where every fourth anion is missing, resulting in a small shift of the ions². The 32 cations occupy two different six-fold coordinated sites. The sites are equipoints "b" and "d", according to international notation³. Eight cations are situated in compressed octahedra (b site) and have six equidistant oxygen atom neighbors at 2.18Å. These oxygen atoms lie approximately at the corners of a cube with two anions missing at opposite vertices⁴. The other 24 cations are at the corners of highly distorted octahedra (d site). For these "d" ions,

there are three possible cation-oxygen distances: 2.13, 2.19 and 2.23Å. In this case, the oxygen atoms are also near the corners of a cube with two empty anions along one face diagonal. Figure 1 shows a schematic representation of the cation sites in In_2O_3 . It is widely accepted that in ITO, tin goes into the In_2O_3 lattice substituting on the indium sites⁵⁻⁶, but the preference of tin for the b site has only recently been proposed⁷⁻⁸.

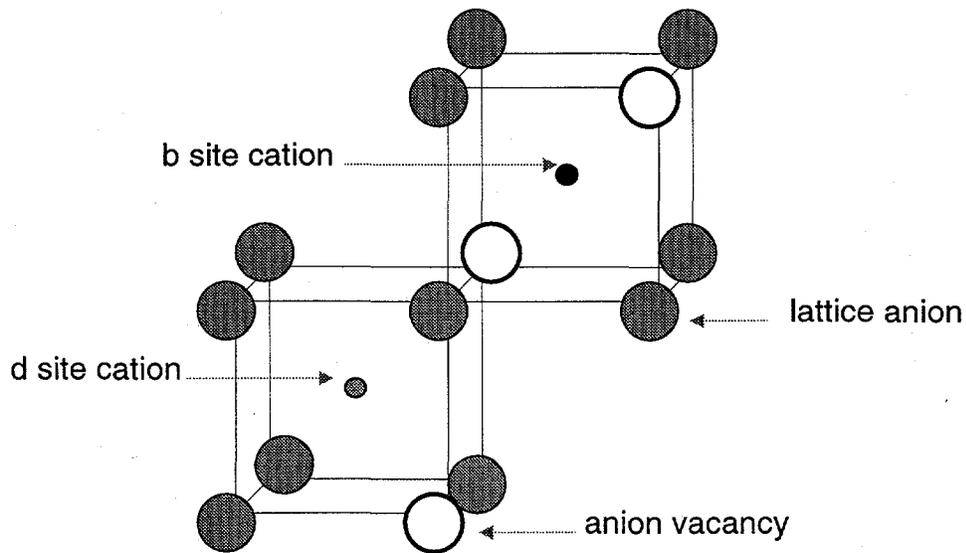


FIGURE 1. Nonequivalent Cation Sites in the Bixbyite Structure

Subbarao et al.⁹ and then De Witt² formulated an anion interstitial model for doped indium oxide type structures. The model consists of completely filled cation sites with an excess of $\delta/2$ anions, O_i'' , which are located at some of the ordered oxygen vacancy sites of In_2O_3 . These interstitial oxygen atoms compensate the charge of the δ ionized tin donors (given the charge of $(\text{Sn}^{4+})_{\text{In}^{3+}}^{\bullet}$). The material can then be formally described as $\text{In}_{2-\delta} \text{Sn}_{\delta}^{\bullet} (\text{O}_i'')_{\delta/2} \text{O}_3$ according to Kröger-Vink notation ($\text{Sn}_{\delta}^{\bullet}$ represents δ tin ions having an effective positive charge of +1, and $(\text{O}_i'')_{\delta/2}$ represents $\delta/2$ oxygen ions on interstitial sites having an effective negative charge of -2). This model was later corroborated and further developed

by the measurements of Frank and Köstlin⁶ who proposed the existence of several defects that are dependent on oxygen partial pressure and tin content. The presence of such defects was deduced from electrical measurements, such as conductivity and mobility. A summary of the defects follows:

At high oxygen partial pressure and large tin doping levels, the defects are mainly $(\text{Sn}_2\text{O}_i^{\bullet})^x$, $(\text{Sn}_2\text{O}_4)^x$, and $((\text{Sn}_2\text{O}_i^{\bullet})(\text{Sn}_2\text{O}_4))^x$.

At very low oxygen partial pressure, the $(\text{Sn}_2\text{O}_4)^x$ defects remain unreduced, while the $(\text{Sn}_2\text{O}_i^{\bullet})^x$ defects get reduced, i.e., the interstitial oxygen atoms are removed leaving Sn^{\bullet} to serve as donors (if p_{O_2} is very low, O_i^{\bullet} disappear and V_O become significant in population).

In the present work, the conductivities of oxidized and reduced ITO samples were measured. Neutron diffraction was used to obtain structural information about the materials as a function of oxygen partial pressure. The diffraction and conductivity results were then compared to the model proposed by Frank and Köstlin.

II. SAMPLE PREPARATION

The starting oxide powders were In_2O_3 99.99% and SnO_2 99.995 + % (Aldrich Chemical Co., Milwaukee, WI). The appropriate amounts of powder were preheated at 600 °C, mixed with acetone in a mortar and pestle, and pressed at 75 MPa. After presintering at 1100 °C, the pellets were reground to homogenize the samples, and pelletized. This heating, grinding and pelletizing sequence was repeated several times. The ground powder was finally mixed with 3 wt. % poly vinyl butyral binder to increase the green density for better pressing. The samples were then pressed at 75 MPa and isostatically cold-pressed at 280 MPa. The binder was removed by heating at 650 °C for three hours using a heating rate of 3 °C/min and a cooling rate of 5 °C/min. After removal of the binder, four specimens (two pure In_2O_3 and two Sn-doped In_2O_3) were sintered at 1350 °C in high-density alumina crucibles. To prevent contamination from the alumina substrate, the pellets were placed on a sacrificial pellet of the same composition. Bar-shaped conductivity/thermopower specimens (4 x 4 x 14 mm) were cut from the pellets using a diamond saw. One pure In_2O_3

and one ITO sample were then subjected to a reduced environment of CO/CO₂ gas ($p_{O_2} \sim 10^{-14}$) for 65 hours at 800 °C. The remaining samples were treated in air for 15 hours at 800 °C. Finally all samples were quenched in air from 800 °C to room temperature.

III. CONDUCTIVITY MEASUREMENTS

Simultaneous conductivity and thermopower measurements were made using a PC-controlled system including a scanner (Model 705, Keithley Instruments, Inc., Cleveland, OH), current source (Model 224, Keithley Instruments, Inc., Cleveland, OH), and a digital multimeter (Model 196, Keithley Instruments, Inc., Cleveland, OH). Four S-type thermocouples (Pt/Pt-10%Rh) were employed using the steady-state gradient technique¹⁰. A current reversal technique was employed to correct conductivity voltages for thermal e.m.f. Thermoelectric coefficients were corrected for the thermopower of platinum. Oxygen partial pressures were controlled using pre-mixed Ar/O₂ mixtures (1 to 10⁻⁵ atm). Below 10⁻⁵ atm, oxygen partial pressures were controlled using CO/CO₂ mixtures and p_{O_2} was measured by a zirconia oxygen cell.

The conductivity for the oxidized ITO was 601 (Ωcm)⁻¹, while for the reduced ITO sample (in CO/CO₂ atmosphere, $P_{O_2} = 10^{-14}$ atm) it was measured to be 1044 (Ωcm)⁻¹. The corresponding thermopowers were -68.7 $\mu\text{V/K}$ and -33.7 $\mu\text{V/K}$. The conductivity and thermopower measurements were performed in-situ at 800 °C. These results are consistent with n-type behavior and carrier contents increasing with reduction.

IV. NEUTRON POWDER DIFFRACTION CHARACTERIZATION

Time of flight (TOF) neutron powder diffraction data were collected on the four powder samples at room temperature using the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory¹¹. Diffraction data were collected on all detector banks. However, only the analysis of data from the high-resolution back-scattering detectors ($\Delta d/d = 0.035$) is presented here. Because the absorption cross-section of indium is significantly large ($\sigma_a = 194$ barns for $\lambda = 1.8\text{\AA}$), an

incident spectrum was collected downstream of the In_2O_3 powder sample. This incident spectrum was used to normalize diffraction data collected for all four powder samples, thus providing a correction for the sample absorption. Model crystal structures were refined by the Rietveld method¹² using the FullProf program¹³.

The results obtained from analyzing the TOF neutron diffraction data using the Rietveld technique are presented in Table I. The second column represents the ideal ion positions for In_2O_3 . During the Rietveld refinement, the thermal parameters of the interstitial oxygen atoms, O_i , were constrained to be the same as those of the lattice anions because it is not possible to refine temperature factors for sites whose occupancies can approach zero. Moreover, within a wide range of values for these temperature factors, the refined O_i site occupancies did not change appreciably.

The Rietveld results are in agreement with Mössbauer results⁷ and recent FLMTO electronic calculations⁸, which show a preference of tin for occupying the b rather than the d site. Another observation is the absence of interstitial oxygen atoms in the pure In_2O_3 samples, and their presence in both ITO samples. The oxidized ITO shows a 2.3 ratio of tin-to-interstitial oxygen, while the reduced ITO exhibits a 5.0 ratio. Both samples were prepared in a similar manner, but the last annealing treatment was performed in a reducing atmosphere, resulting in the loss of some interstitial oxygen and an increased conductivity.

The 2.3 tin-to-interstitial oxygen ratio in the oxidized sample may corroborate the presence of complex defects formed by tin and oxygen atoms postulated by Frank and Köstlin. As mentioned before, the "reducible" defects $(\text{Sn}_2\text{O}_i)^\times$ are thought to be formed by two tin atoms and an oxygen interstitial (2:1 tin-to-interstitial ratio), and upon decreasing the oxygen partial pressure these get reduced, freeing up the Sn^\bullet defects which contribute to an increase in the conductivity. Furthermore, the tin-to-interstitial oxygen ratio would be expected to increase as observed. It should be pointed out that the non-reducible $(\text{Sn}_2\text{O}_4)^\times$ defect species postulated by Frank and Köstlin involves one interstitial and three lattice oxygen atoms (maintaining a tin-to-interstitial oxygen ratio of 2:1). This means that they contribute to the measured Sn concentrations, but do not affect the carrier concentrations.

Therefore, any interstitial oxygen atoms that participate in such non-reducible defects would remain present even at low oxygen partial pressures, as observed.

TABLE I. Structural Results and Refinement Parameters Obtained from Rietveld Refinement of TOF Neutron Powder Diffraction Data

	Ideal In ₂ O ₃	Oxidized In ₂ O ₃	Reduced In ₂ O ₃	Oxidized ITO	Reduced ITO
Cation b					
x	1/4	1/4	1/4	1/4	1/4
y	1/4	1/4	1/4	1/4	1/4
z	1/4	1/4	1/4	1/4	1/4
B (Å ²)		0.471(31)	0.385(28)	0.475(35)	0.483(33)
Fraction Sn				0.135(39)	0.154(34)
Cation d					
x	0.4666	0.4663(1)	0.4664(1)	0.4677(2)	0.4669(1)
y	0	0	0	0	0
z	1/4	1/4	1/4	1/4	1/4
B (Å ²)		0.310(10)	0.356(9)	0.326(11)	0.346(9)
Fraction Sn				0.021(19)	0.016(16)
Lattice oxygen					
x	0.3909	0.3905(1)	0.3905(1)	0.3901(1)	0.3903(1)
y	0.1544	0.1548(1)	0.1546(1)	0.1541(1)	0.1545(1)
z	0.3814	0.3818(1)	0.3819(1)	0.3818(1)	0.3817(1)
B (Å ²)		0.506(24)	0.492(23)	0.537(29)	0.532(25)
Interstitial oxygen					
x	1/8			0.0878(23)	0.0839(41)
y	1/8			0.0878(23)	0.0839(41)
z	1/8			0.0878(23)	0.0839(41)
B (Å ²)		0.506(24)*	0.492(23)*	0.537(29)*	0.532(25)*
Fraction O _i		-0.007(7)	0.001(4)	0.042(6)	0.020(5)
Refinement parameters					
R _p (%)		7.19	7.22	7.66	6.62
R _{wp} (%)		4.96	4.88	5.50	4.73
χ ²		1.29	1.35	1.75	1.56
Sn /O _i					
a (Å)		10.1208(1)	10.1203(1)	2.3	5.0
				10.1252(1)	10.1312(1)

*B(O_{interstitial}) fixed to B(O_{lattice}) during the refinement.

Several authors^{1, 6-7, 14-15} report an increased lattice parameter with tin concentration (for cation fractions of Sn greater than 2 at. %) and with decreasing oxygen partial pressure. These trends were also observed in this study. The 5 at. % Sn-doped In_2O_3 samples exhibit a greater lattice parameter than the pure In_2O_3 samples. The reduced ITO also presents a lattice constant larger than that of the oxidized ITO.

IV. CONCLUSIONS

When tin is introduced into the In_2O_3 lattice, it prefers to go into the less distorted b cation site. This substitution of tin for indium creates a charge imbalance, which results in the partial filling of anion vacancies. The tin-to-interstitial oxygen ratio in the oxidized ITO (2.3) is very close to that proposed by Frank and Köstlin due to the existence of defect complexes $(\text{Sn}_2^{\bullet}\text{O}_i^{\prime\prime})^{\times}$ made up of two tins and one interstitial oxygen. Upon decreasing the oxygen partial pressure, these complexes get reduced, freeing up some of the Sn^{\bullet} defects, which results in a higher conductivity, and a smaller interstitial oxygen population. However, the presence of interstitial oxygen atoms in the reduced sample may be attributed to the presence of some non-reducible defects $(\text{Sn}_2\text{O}_4)^{\times}$ which become more important at low oxygen partial pressure. Both ITO samples exhibited an increased lattice parameter as compared to pure In_2O_3 . Furthermore, the reduced ITO sample presented a greater lattice constant than that of the oxidized ITO sample. Both changes in the lattice parameter agree with observations reported previously in the literature.

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REFERENCES

- 1) J.C.C.FAN and F.J.BACHNER, *J. Electrochem. Soc.* **122**(1975)1719.
- 2) J.H.W.DE WITT, *J. Solid State Chem.* **20**(1977)143.
- 3) A.J.C.WILSON, ed., *The International Union of Crystallography, International Tables for Crystallography* (Kluwer Academic Publishers, Dordrecht, The Netherlands) 1992.
- 4) M.MAREZIO, *Acta Cryst.* **20**(1966)723.
- 5) H.KÖSTLIN, R.JOST, and W.LEMS, *Phys. Status Solidi A* **29**(1975)87.
- 6) G.FRANK and H.KÖSTLIN, *Appl. Phys. A* **27**(1982)197.
- 7) N.NADAUD, N.LEEQUEUX, M.NANOT, J.JOVE, and T.ROISNEL, *J. Solid State Chem.* **135**(1998)140.
- 8) O.N.MRYASOV and A.J.FREEMAN, "Transparent Conducting Behavior of the Doped In and Tl oxides: Role of Dopant and Host", American Physical Society Annual Meeting, Minneapolis, MN, abstract B9.004, March 20, 2000.
- 9) E.C.SUBBARAO, P.H.SUTTER, and J.HRIZO, *J. Am. Ceram. Soc.* **48**(1965)443.
- 10) A.TRESTMAN-MATTS, S.DORRIS, and T.O.MASON, *J. Am. Ceram. Soc.* **66**(1983)589.
- 11) J.D.JORGENSEN, J.FABER, J.M.CARPENTER, R.K.CRAWFORD, J.R.HAUMANN, R.L.HITTERMAN, R.KLEB, G.E.OSTROWSKI, F.J.ROTELLA, and T.G.WORLTON, *J. Appl. Cryst.* **22**(1989)321.
- 12) H.RIETVELD, *J. Appl. Cryst.* **2**(1969)65.
- 13) J.RODRÍGUEZ-CARVAJAL, Reference Guide for the Computer Program FullProf, Laboratoire Leon Brillouin, CEA-CNRS, Saclay, France (1997).
- 14) K.L.CHOPRA, S.MAJOR, and D.K.PANDYA, *Thin Solid Films* **102**(1983)1.
- 15) Ph.PARENT, H.DEXPERT, G.TOURILLON, and J.M.GRIMAL, *J. Electrochem. Soc.* **139**(1992)276.