

Defect Structure Studies on Bulk Indium-Tin Oxide

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Introduction

The goal of the study is to investigate the defect structure of Sn-doped In₂O₃, also known as indium-tin oxide (ITO). ITO materials are widely used as transparent electrodes in flat-panel displays, energy-efficient windows, and solar cells [1]. Understanding the defect chemistry of ITO is important for improving and developing this and other transparent conductor materials.

ITO exhibits a fluorite-derived structure: the cubic bixbyite or C-type rare-earth sesquioxide structure, Ia3 space group (number 206). Bixbyite has two different sixfold coordinated cation sites, and only three fourths of the anions found in fluorite are present. Figure 1 shows the two cation sites, which are referred to as equipoints *b* and *d* [2]. The *b* site cations have six equidistant oxygen anion neighbors at 2.18 Å that lie approximately at the corners of a cube with two anion vacant sites (referred to as oxygen interstitial sites) along one body diagonal [3]. The *d* site cations are coordinated to six oxygen anions at three different distances: 2.13, 2.19, and 2.23 Å. These oxygen anions are near the corners of a distorted cube with two empty interstitial sites along one face diagonal.

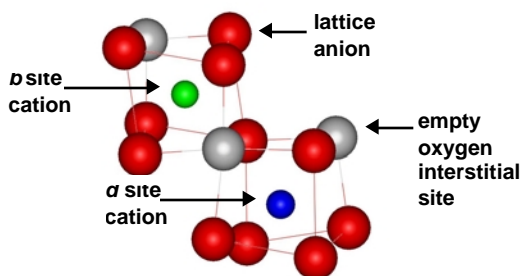
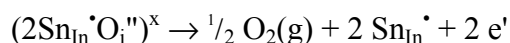


FIG. 1. Cation sites in ITO.

Frank and Köstlin inferred a defect model of ITO from measured electrical properties [4]. The model describes ITO as In_{2- δ} Sn _{δ} (O_i^{''}) _{$\delta/2$} O₃ and consists of completely filled cation sites and additional $\delta/2$ O_i^{''} anions found at some of the initially vacant anion sites in In₂O₃. These so-called “interstitial anions” charge-compensate the δ ionized tin donors [given the charge of the (Sn⁴⁺)_{In3+} species], which go into the

indium sites. Frank and Köstlin [4] further proposed that the tin and interstitial oxygens are found in 2:1 (i.e., 2 tins and 1 oxygen interstitial) neutral defect associates whose concentrations depend on oxygen partial pressure and tin content. The reducible (2Sn_{In}[•]O_i^{''})^x associate has two nonadjacent Sn⁴⁺ ions and an oxygen interstitial anion and is a loosely bound cluster that decomposes upon reduction as follows:



The electrons that charge-compensate the Sn_{In}[•] species increase the conductivity in reduced ITO samples. On the other hand, the nonreducible defect (2Sn_{In}[•]3O_oO_i^{''})^x is a tightly bound cluster formed by two Sn⁴⁺ cations on nearest-neighbor sites, three lattice oxygen ions, and one oxygen interstitial anion. This defect exists even under reducing conditions and ties in the Sn_{In}[•] species, resulting in an unchanged conductivity even when more Sn dopant is added to the structure.

Warchkow et al. [5, 6] developed a defect model for ITO based on theoretical calculations. The model is similar to Frank and Kostlin’s, except for two major differences. The Warchkow model does not find two types of 2:1 structurally different associated defects, and it predicts that the nonreducibility of O_i^{''} species results from the aggregation of two or more Sn-O_i clusters.

To study the defect structure of ITO, the cation distribution and the presence of interstitial anions are extremely important. Given the proximity of In and Sn in the periodic table, their x-ray scattering factors are similar. In order to distinguish them, x-ray energies near the absorption edges were used to maximize their contrast. Structural information on oxygen and accurate Debye-Waller factors were obtained from time-of-flight (TOF) neutron diffraction experiments. The synchrotron and neutron diffraction data were combined to fully investigate the defect structure. In a previous APS activity report [7], we presented our results for nano-ITO materials. The present report includes new results on the defect structure of bulk-ITO materials.

Methods and Materials

The starting materials were 99.99% In₂O₃ and 99.995% SnO₂ (Aldrich Chemical Co., Milwaukee,

WI). Pellets having 5-wt% SnO₂ and 95% In₂O₃ were pressed, presintered at 1100°C, and ground several times to achieve homogenization. Ground powder was mixed with 3-wt% polyvinylbutyral binder and pressed into pellets at 75 MPa and isostatically cold-pressed at 280 MPa. The binder was removed by being heated at 650°C for 3 hours. All samples were embedded in sacrificial powder of the same composition and sintered at 1350°C in high-density alumina crucibles. Bars of 4 × 4 × 14 mm were cut from the pellets. One pure In₂O₃ and one ITO sample were reduced in CO/CO₂ gas for 65 hours at 800°C. The other pure In₂O₃ and ITO samples were annealed in air for 8 hours at 800°C. All samples were quenched in air to room temperature.

Simultaneous four-point electrical conductivity and thermopower were measured as described in Ref. 7. The electrical measurements were taken *in situ* at 800°C on ITO samples.

TOF neutron powder diffraction data were collected at room temperature from the high-resolution backscattering detectors ($\Delta d/d = 0.0035$) of the special environment powder diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne [8]. The high sample absorption (due to the large indium absorption cross section: $\sigma_a = 194$ barns for $\lambda = 1.8$ Å) was experimentally corrected by normalizing the diffraction data of all samples by an incident spectrum collected downstream of the In₂O₃ powder sample.

Synchrotron, high-resolution, powder diffraction data were also collected on the same samples at DND-CAT beamline station. 5-BM-C, which is equipped with a two-circle diffractometer, a Ge(220) analyzer crystal, and vertical Soller slits, resulting in high-resolution diffraction data ($\Delta d/d = 0.0006$ for bulk powders at 28 keV). The powders, which were loaded in glass capillary tubes, were run in transmission mode at the In K edge (27,940 eV) and 100 eV below it (27,840 eV) to maximize the contrast of the In and Sn cations. The anomalous f' and f'' scattering correction factors at both energies were experimentally obtained by analyzing extended x-ray absorption fine structure (EXAFS) scans of the same samples with the program Chooch [9]. The two x-ray diffraction patterns combined with the TOF neutron diffraction data were analyzed with Rietveld refinement [10] by using the program FullProf [11].

Results

The *in situ* (measured at 800°C) conductivity for oxidized ITO was 500 (Ωcm)⁻¹, and for the CO/CO₂ reduced ITO sample ($p_{\text{O}_2} \sim 10^{-14}$ atm), it increased to 1690 (Ωcm)⁻¹. The corresponding thermopowers were -75 $\mu\text{V/K}$ and -34 $\mu\text{V/K}$.

Table 1 summarizes the structural results obtained from the combined Rietveld analysis of x-ray and neutron diffraction data.

Discussion

The electrical conductivity and thermopower results confirm that the carrier concentration increases with reduction, as expected for an n-type material. The Rietveld results suggest that, in agreement with Mössbauer experiments [12, 13] and previous Rietveld results for nano-ITO materials [7], tin prefers to occupy the *b* cation site. Since the Sn concentration in bulk-ITO materials is small (compared to nano-ITO, where Sn doping can be three times higher), the uncertainties in the cation distributions are larger than for nano-ITO.

TABLE 1. Structural results obtained from the combined Rietveld refinement of x-ray and neutron diffraction patterns.

	In ₂ O ₃	ITO air	ITO CO/CO ₂
<i>Cation b</i> ($x = y = z = 1/4$)			
B (Å ²)	0.441(55)	0.404(47)	0.369(51)
Sn		0.059(32)	0.090(33)
—			
In+Sn			
<i>Cation d</i> ($y = 0, z = 1/4$)			
B (Å ²)	0.337(32)	0.328(24)	0.257(26)
x	0.4662(1)	0.4673(1)	0.4670(1)
Sn		0.018(11)	0.008(11)
—			
In+Sn			
<i>O_s</i> (structural oxygen)			
B (Å ²)	0.533(26)	0.534(23)	0.473(25)
x	0.3904(1)	0.3901(2)	0.3902(1)
y	0.1549(1)	0.1541(1)	0.1545(1)
z	0.3819(1)	0.3820(1)	0.3818(1)
<i>O_i</i> (interstitial oxygen)			
x	0.080	0.086(3)	0.080(5)
O _i fraction	-0.008(5)	0.026(5)	0.010(5)
total Sn %		2.9	2.9
Sn/O _i		2.2(4)	5.5(2.4)
a (Å)	10.1216(1)	10.1250(2)	10.1327(2)
<i>Refinement parameters</i>			
R _{Bragg-x-ray}	5.07	2.68	1.70
R _{Bragg-x-ray}		5.44	8.60
R _{Bragg-neutron}	2.04	4.28	5.44
χ^2	1.43	1.60	1.58

The absence of interstitial oxygen anions in the pure In_2O_3 samples and their presence in both bulk-ITO samples are also observed as seen in nano-ITO materials.

The presence of $(2\text{Sn}_{\text{In}}\cdot\text{O}_i)^x$ -associated defects postulated by Frank and Köstlin [4] and Warschkow et al. [5, 6] is supported by the measured ratio of tin to interstitial oxygen of 2.2 ± 0.4 in the oxidized ITO (since these defects are believed to have two tin cations and one oxygen interstitial anion; i.e., 2:1 $\text{Sn}:\text{O}_i$ ratio). The ratio of $\text{Sn}:\text{O}_i$ increases during reduction as a result of the removal of some O_i species (and thus the freeing up of electrons). At the same time, the electrical conductivity and carrier concentration are expected to increase, as observed in the present experiment. The presence of an interstitial oxygen population in highly reduced samples supports the irreducibility of some O_i species.

Previous reports found that lattice parameter increased with Sn doping and with decreasing oxygen partial pressure [1, 4, 7, 13]. These trends were also observed in these experiments. The increase in the lattice parameter with Sn doping is attributed to the charge repulsion among Sn cations, arising from the incomplete charge-compensation by oxygen interstitial anions. Therefore, decreasing the oxygen partial pressure and removing oxygen interstitial anions further expands the lattice parameter of the ITO material.

Acknowledgments

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