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Symmetry-induced transparency in conductive metal oxides for optoelectronics

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The coexistence of optical transparency and electrical conductivity in In_2O_3 relies on an intricate synergy of the underlying crystal symmetry, conduction-band energy, and doping efficiency.

The unification of optical transparency and electronic conductivity in metal oxides produces a special class of rare materials, transparent conductive oxides (TCOs). This combination of physical properties makes them essential components for optoelectronic applications, including photovoltaic and photoelectrochemical devices, LCDs, and LEDs (see Figure 1). Although the unique chemistry of TCOs has been investigated extensively since the mid-20th century, the ultimate question—What factors produce an optimal TCO?—has no certain answer. As we strive for increased light-to-current conversion rates in solar cells and improved efficiencies in electronic devices, complete knowledge and control of these material functionalities is imperative.

Indium sesquioxide (In_2O_3) is the prototypical n-type TCO, exhibiting excellent carrier mobilities (>100cm^2/Vs) coupled with an optical band gap outside the visible range (>3.2eV). For the past 40 years, the magnitude and nature of the electronic band gap has been debated. By taking into account the underlying In_2O_3 crystal symmetry combined with high-resolution x-ray spectroscopy, we have reached a revised understanding of its electronic structure.[1] This provides new insight into both the essential ingredients for a good TCO and the design strategy needed for maximizing future performance.

To address the underlying electronic structure of In_2O_3, we employ two approaches. First, we conduct first-principles electronic-structure calculations based on density-functional theory. This enables access to the distribution of electrons within a system and, as such, to all ground-state properties. We then perform symmetry analysis on the resulting band structure to understand the nature of the bonding and optical properties. We subsequently investigate the doped and defective electronic-structure behavior.[2] At the same time, our experimental collaborators have grown high-quality epitaxial In_2O_3 samples[3] and performed a series of high-resolution synchrotron-based spectroscopic measurements (soft and hard x-ray photoemission and soft x-ray emission).[1]

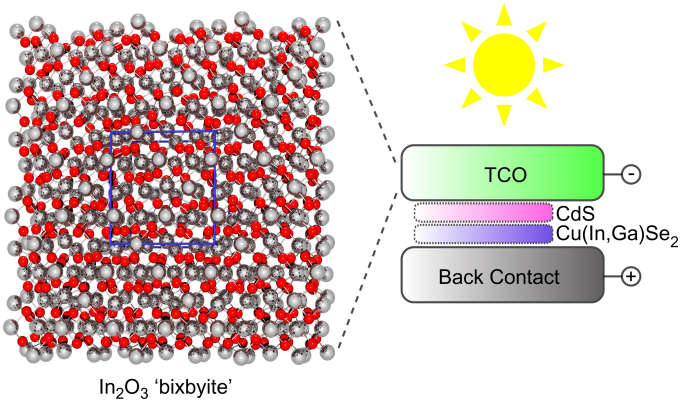

Figure 1. *Crystal structure of indium sesquioxide (In_2O_3) and a schematic of a typical thin-film solar cell. TCO: Transparent conductive oxide.*

From in-depth symmetry analysis of the In_2O_3 band structure we came across a surprising discovery: band-edge transitions are parity forbidden. As both the states at the top of the valence band and bottom of the conduction band are of even parity, dipole transitions cannot occur between them. In fact, comprehensive optical analysis revealed that strong optical transitions occur only from 0.8eV below the top of the valence band. Predictions that the electronic and optical band gaps in In_2O_3 are inequivalent were validated unequivocally when a combination of independent spectroscopic measurements found that the In_2O_3 electronic band gap is indeed less than 3eV (see Figure 2).[1] This is in stark contrast to the previously assumed band gap (3.75eV).

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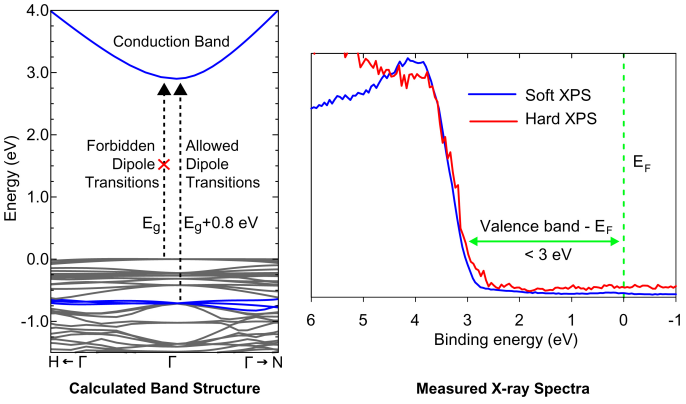

Figure 2. Calculated density-functional theory band structure of In_2O_3 and experimental x-ray spectra relative to the Fermi energy, E_F, at the bottom of the conduction band. E_g: Band-gap energy. XPS: X-ray photoemission strength.

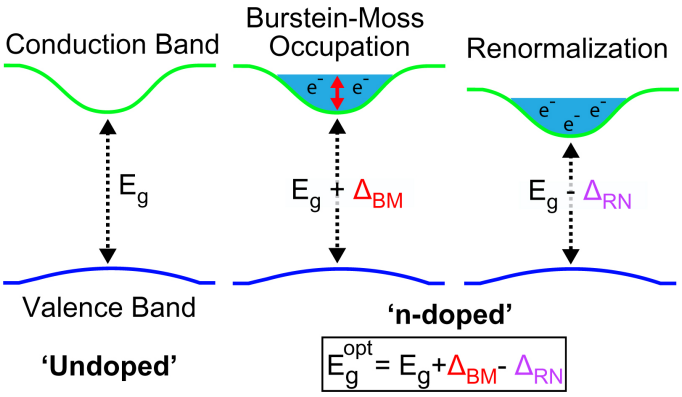

Figure 3. Schematic changes in the conduction band contributing to optical band-gap (E_g^{opt}) changes on addition of electrons. Δ_{BM}: Change due to Burstein–Moss occupation. Δ_{RN}: Deviation caused by renormalization.

Both the magnitude of the electronic band gap and the absolute band-edge positions are key attributes in determining material performance in optoelectronic devices. The band offsets between two components determine their charge-transport behavior. As most oxides deviate from their formal chemical composition (e.g., $In_2O_{3-\delta}$), the resulting high intrinsic-carrier concentrations ($10^{20}cm^{-3}$) make it difficult to determine the underlying band gaps. This arises from occupation of the lower conduction band and movement of the band edges on addition of carriers, leading to renormalization (see Figure 3). By simulating n-type In_2O_3, we provided a quantitative estimation of these contributions.[2] We have demonstrated a direct correspondence between the chemical nature of the donor defects and the magnitude of renormalization. Coupled with the experimental data, this corresponds to a re-evaluation of the In_2O_3 intrinsic band gap to 2.67eV.[3]

The small band-gap energy of In_2O_3 is, somewhat paradoxically, a major factor in determining its excellent TCO performance. The low conduction-band position—driven by relativistic contraction of the In 5s orbital—means that the Fermi-level pinning energy lies above the conduction-band minimum.[4] This is remarkable and ensures that In_2O_3 can support high electron concentrations without forming compensating acceptor defects, even when heavily doped.[5] Other TCOs with higher band-gap (conduction-band) energies (e.g., ZnO 3.44eV, SnO_2 3.60eV) cannot match the low resistivity of In_2O_3.

In conclusion, an optimal TCO should have both a small fundamental electronic band gap (low conduction band for n-type or high valence band for p-type TCOs) and a large optical band gap (to limit visible-light absorption). In_2O_3 maintains optical transparency through dipole forbidden band-edge transitions, despite having a fundamental electronic band gap in the blue range. We are now pursuing more complex multicomponent crystalline TCOs such as $InXO_3(ZnO)_n$ (where X represents In, Ga, or Al).[6] Our preliminary work indicates that the intrinsic properties of the binary components have a strong role to play in these materials and offer a definite avenue for improving future TCO performance.

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