

PbO₂: from semi-metal to transparent conducting oxide by defect chemistry control

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Lead dioxide has been studied for over 150 years as a component of the lead-acid battery. Based on first-principles calculations, we predict that by tuning the concentration of electrons in the material, through control of the defect chemistry, PbO₂ can be rendered from black to optically transparent, thus opening up applications in the field of optoelectronics.

Transparent conducting oxides (TCOs) are compounds which combine the normally mutually exclusive properties of transparency and conductivity. Most transparent materials, such as glass, behave as electrical insulators with high resistivities of $>10^{10} \Omega \text{ cm}$, whereas materials with low resistivities (10^{-4} – $10^{-7} \Omega \text{ cm}$), such as metals, do not transmit visible light. The combination of both properties in a single material is thus an unusual phenomenon and TCOs have proved indispensable in the development of optoelectronic devices such as solar cells, flat panel displays and light emitting diodes.^{1–4} At present, the industry standard n-type TCO is In₂O₃:Sn (ITO) which usually demonstrates conductivities of $\sim 10^4 \text{ S cm}^{-1}$, whilst retaining $>90\%$ transparency in the visible range.⁵ The overwhelming demand for ITO, coupled with the low abundance of indium within the earth's crust has made indium an increasingly expensive commodity, which has led to a large research drive to find viable alternative materials.⁶

There exist two distinct classes of TCO: (i) wide band gap TCOs (WB-TCO), and (ii) narrow band gap TCOs (NB-TCO), as illustrated in Fig. 1. A WB-TCO is characterized by a large fundamental band gap, usually greater than 3 eV, making the stoichiometric material transparent to visible light, e.g. ZnO and SnO₂.⁷ To enhance intrinsic n-type conductivity in these materials, itself the result of oxygen sub-stoichiometry,

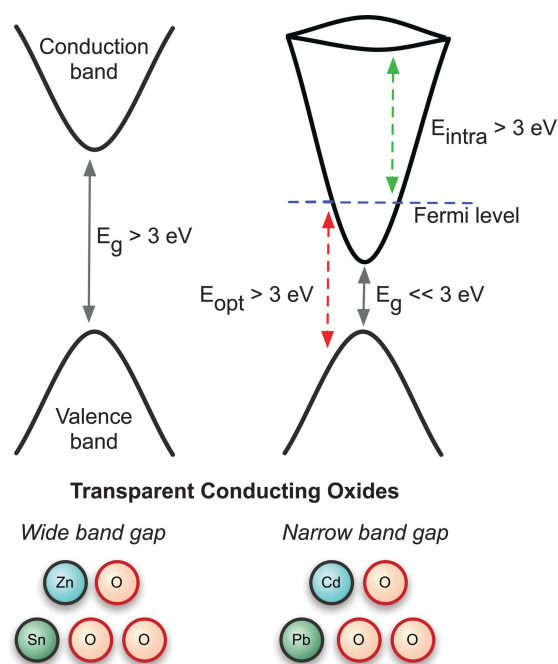


Fig. 1 Schematic of a (a) wide gap and (b) narrow gap TCO, where the Fermi level refers to the electron chemical potential for heavily doped n-type materials.

the electron carrier concentrations can be further increased by suitable extrinsic donor doping.⁸

An NB-TCO, on the other hand, is coloured or black when close to stoichiometric. However, when donor doped to high carrier concentrations, optical transparency can be achieved through the blue-shift of the optical band gap following the Moss–Burstein^{9,10} effect (E_{opt} in Fig. 1). A known example of this is CdO, where the fundamental band gap is less than 1 eV, and the optical band gap of the electron rich material can be greater than 3 eV.^{11–14} To ensure optical transparency in the electron rich material, transitions from the filled conduction band states to the next highest conduction band (E_{intra} in Fig. 1) should also lie above the threshold for visible light absorption.^{15,16}

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Another potential limitation is the absorption or reflection of light by free carriers, which fortuitously occurs in the infra-red range for these materials.⁷

Upon moving down group 12 from Zn to Cd, there is a transition from WB-TCO (ZnO) to NB-TCO (CdO). It follows that the same relationship may also hold for group 14 from Sn to Pb. SnO₂ is a known WB-TCO; however, the physical properties of PbO₂ are not well understood.^{17–23} It has recently been demonstrated that despite its high electrical conductivity, PbO₂ is a narrow band gap semiconductor that has a preference for oxygen sub-stoichiometry, which results in carrier concentrations greater than 10²¹ cm^{−3}.²⁴ The question therefore arises as to whether the electron concentration of PbO₂ and related narrow band gap oxides can in principle be tuned into the regime for simultaneous transparency and conductivity?

We have performed first principles calculations on β-PbO₂ (the mineral Plattnerite), the stable rutile phase of PbO₂. The method is based on density functional theory (the hybrid HSE06²⁵ functional) as implemented in the code VASP.^{26,27} The projector-augmented wave^{28,29} method was used to describe the interactions between the cores (Pb:[Kr] and O:[He]) and the valence electrons. Both the plane wave basis set and *k*-point sampling were rigorously checked for convergence (29.40 Ry cut-off and a *k*-point grid of 6 × 6 × 4). The optimized structural parameters were found to be within 1% of neutron diffraction measurements.²⁴

The calculated band diagram for PbO₂ is shown in Fig. 2(a). Despite the small indirect band gap of 0.23 eV, it is evident that at high carrier concentrations (for an electron chemical potential ~2.3 eV above the top of the valence band) a window for transparency emerges. The window is widened by considering the recent report that transitions from the upper valence band are symmetry forbidden. The inversion symmetry of the lattice imposes Laporte selection rules,²⁴ and strong optical transitions to the conduction band commence only from 0.7 eV below the valence band maximum, similar to the high performance TCO In₂O₃. This relationship is quantified in Fig. 2(b), where the effective optical band gap is plotted as a function of the electron concentration, explicitly taking into account the contributions of both inter- and intra-band transitions.

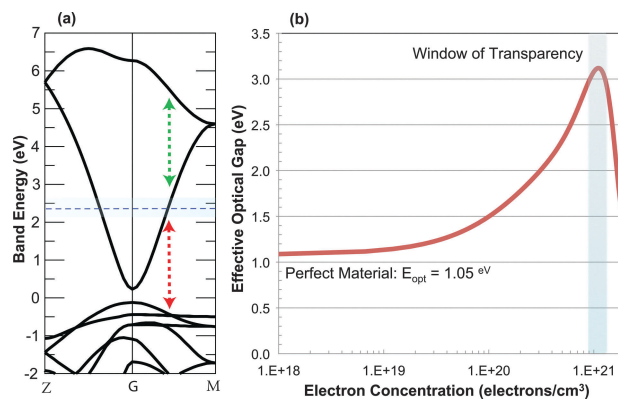
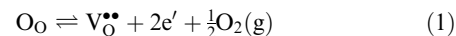


Fig. 2 (a) Band structure diagram of PbO₂ illustrating the optical and intra-band transitions and (b) effective optical band gap plotted as a function of electron carrier concentration.

From this model, which is calculated based on the Moss–Burstein occupation, optical transparency is achievable for carrier concentrations in the range of 9.14×10^{20} to 1.07×10^{21} cm^{−3}.

Typical carrier concentrations of the order of 1.5×10^{21} cm^{−3} are reported for PbO₂ samples,^{21,30} which have been confirmed to be due to the facile formation of oxygen vacancies,²⁴ according to the defect reaction:



These carrier concentrations are prohibitively high, and effectively “close” the window for transparency by lowering E_intra below 3 eV. To “reopen” the window, it is therefore necessary to reduce the electron concentration. From the previous relationship we can see that the equilibrium concentration of oxygen vacancies (electrons) is related to the oxygen partial pressure, P_O_2 , and hence can be controlled by annealing under different gaseous environments. However, no study of the dependence of optical band gap or electron concentration with gaseous partial pressures has been reported to our knowledge. Following the law of mass action, the equilibrium constant K_c obeys:

$$K_\text{c} = [\text{V}_\text{O}^{\bullet\bullet}][\text{e}']^2 P_\text{O}_2^{-\frac{1}{2}}, \quad (2)$$

which, assuming the charge neutrality relation $[\text{V}_\text{O}^{\bullet\bullet}] = 2[\text{e}']$, results in a predicted dependence of the electron concentration (conductivity) on $P_\text{O}_2^{-\frac{1}{6}}$.

An alternative approach to reducing the carrier concentration would be to intentionally dope the material with acceptor impurities. The incorporation of trivalent metals could be used to quench mobile electron carriers. Taking the example of Bi-doping:



A lowering of the carrier concentration due to Bi-doping of PbO₂ has been reported previously,^{31,32} and the same approach has been successful in lowering the carrier concentration of other TCO materials.^{33,34} An additional benefit of reducing the carrier concentration should be an increase in electron mobility, and hence conductivity, which is a critical performance indicator.³⁵

Due to the relative abundance and lower cost of Pb compared to In, successful modulation of the carrier concentration in PbO₂, and realisation of optical transparency, could have applications in the optoelectronics industry in the near-term as viable replacements for high-cost ITO contacts are required. Further investigation of the PbO₂ system is therefore warranted in order to verify our predictions.

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References

- 1 G. Thomas, *Nature*, 1997, **389**, 907.
- 2 B. J. Ingram, G. B. Gonzalez, D. R. Kammler, M. I. Bertoni and T. O. Mason, *J. Electroceram.*, 2004, **13**, 167–175.
- 3 K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano and H. Hosono, *Nature*, 2002, **419**, 462–465.
- 4 T. Minami, *Semicond. Sci. Technol.*, 2005, **20**, S35–S44.
- 5 R. G. Gordon, *MRS Bull.*, 2000, **25**, 52–57.
- 6 J. J. Berry, D. S. Ginley and P. E. Burrows, *Appl. Phys. Lett.*, 2008, **92**, 193304.
- 7 P. P. Edwards, A. Porch, M. O. Jones, D. V. Morgan and R. M. Perks, *Dalton Trans.*, 2004, 2995.
- 8 A. Walsh, J. L. F. Da Silva and S. H. Wei, *Phys. Rev. B*, 2008, **78**, 075211.
- 9 N. F. Mott, *Rev. Mod. Phys.*, 1968, **40**, 677–683.
- 10 P. P. Edwards and M. J. Sienko, *Phys. Rev. B*, 1978, **17**, 2575–2581.
- 11 M. Burbano, D. O. Scanlon and G. W. Watson, *J. Am. Chem. Soc.*, 2011, **133**, 15065.
- 12 S. K. Vasheghani Fahrahani, T. D. Veal, P. D. C. King, J. Zúñiga-Pérez, V. Muñoz-Sanjóe and C. F. McConville, *J. Appl. Phys.*, 2011, **109**, 073712.
- 13 S. Jin, Y. Yang, J. E. Medvedeva, J. R. Ireland, A. W. Metz, J. Ni, C. R. Kannewurf, A. J. Freeman and T. J. Marks, *J. Am. Chem. Soc.*, 2004, **126**, 13787–13793.
- 14 Y. Yang, S. Jin, J. E. Medvedeva, J. R. Ireland, A. W. Metz, J. Ni, M. C. Hersam, A. J. Freeman and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 8796–8804.
- 15 C. Kilic and A. Zunger, *Phys. Rev. Lett.*, 2002, **88**, 095501.
- 16 D. Segev and S. H. Wei, *Phys. Rev. B*, 2005, **71**, 125129.
- 17 D. Raviendra, *Phys. Rev. B*, 1986, **33**, 2660–2664.
- 18 L. M. Peter, *Surf. Sci.*, 1980, **101**, 162.
- 19 D. A. Frey and H. E. Weaver, *J. Electrochem. Soc.*, 1960, **107**, 930.
- 20 L. A. Boyarskii, S. P. Gabuda, S. G. Kozlova and R. N. Pletnev, *Low Temp. Phys.*, 2002, **28**, 691–694.
- 21 D. J. Payne, R. G. Egdell, W. Hao, J. S. Foord, A. Walsh and G. W. Watson, *Chem. Phys. Lett.*, 2005, **411**, 181–185.
- 22 D. J. Payne, R. G. Egdell, D. S. L. Law, P. A. Glans, T. Learmonth, K. E. Smith, J. H. Guo, A. Walsh and G. W. Watson, *J. Mater. Chem.*, 2007, **17**, 267–277.
- 23 D. J. Payne, R. G. Egdell, G. Paolicelli, F. Offi, G. Panaccione, P. Lacovig, G. Monaco, G. Vanko, A. Walsh, G. W. Watson, J. Guo, G. Beamson, P. A. Glans, T. Learmonth and K. E. Smith, *Phys. Rev. B*, 2007, **75**, 153102.
- 24 D. O. Scanlon, A. B. Kehoe, G. W. Watson, M. O. Jones, W. I. F. David, D. J. Payne, R. G. Egdell, P. P. Edwards and A. Walsh, *Phys. Rev. Lett.*, 2011, **107**, 246402.
- 25 S. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207–8215.
- 26 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 27 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251–14271.
- 28 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.
- 29 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 30 J. P. Pohl and G. L. Schlectriemen, *J. Appl. Electrochem.*, 1984, **14**, 521–531.
- 31 S. Rothenberg, D. J. Payne, A. Bourlange and R. G. Egdell, *J. Appl. Phys.*, 2007, **102**, 113717.
- 32 W. T. Fu and H. C. F. Martens, *Solid State Commun.*, 2000, **115**, 423–426.
- 33 T. Nagata, O. Bierwagen, M. E. White, M. Y. Tsai, Y. Yamashita, H. Yoshikawa, N. Ohashi, K. Kobayashi, T. Chikyow and J. S. Speck, *Appl. Phys. Lett.*, 2011, **98**, 232107.
- 34 D. O. Scanlon and G. W. Watson, *J. Mater. Chem.*, 2012, **22**, 25236–25245.
- 35 D. Slocombe, A. Porch, M. Pepper and P. P. Edwards, *Energy Environ. Sci.*, 2012, **5**, 5387–5391.