Combining high conductivity with complete optical transparency: A band structure approach

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Abstract. – A comparison of the structural, optical and electronic properties of the recently discovered transparent conducting oxide (TCO), nanoporous $Ca_{12}Al_{14}O_{33}$, with those of the conventional TCOs (such as Sc-doped CdO) indicates that this material belongs conceptually to a new class of transparent conductors. For this class of materials, we formulate criteria for the successful combination of high electrical conductivity with *complete* transparency in the visible range and emphasize the significant correlation between their structural characteristics and electronic and optical properties. Our analysis suggests that this set of requirements can be met for a group of novel materials called electrides which may have desired features such as connected structural cavities, large bandgaps and near-metallic electronic conductivity.

Transparent conducting oxides (TCO) have been known for almost a century [1] and employed technologically for decades. Today, the area of practical applications of this special class of materials which can simultaneously act as a window layer and as an electrically conducting contact layer, is very large [2–4]: it includes optoelectronics (invisible circuits), flat-panel displays, energy supply (solar cells) and energy conservation ("smart" windows) devices. The commercial demand for less expensive, more flexible, environmentally friendly materials that exhibit both high optical transmission and electrical conductivity continues to stimulate further research.

All well-known and widely used TCOs (such as In, Sn, Zn, Cd, Ga and Cu oxides and their blends) share similar chemical, structural and electronic properties as well as carrier generation mechanisms. These oxides of post-transition (or transition) metals have relatively close-packed structure with four- or six-fold coordinated metal ions. Upon introduction of native or substitutional dopants, they show high transparency in the visible range (~ 80–90%) and high electrical conductivity (up to $\sim 10^4 \, \mathrm{S/cm}$). Common to all known TCOs, a highly dispersed band at the bottom of the conduction bands is the most important feature of the host electronic band structure. It provides both i) the high mobility of the extra carriers (electrons) due to their small effective masses and ii) low optical absorption due to a pronounced Burstein-Moss shift which helps to keep intense interband transitions out of the visible range [5].

To illustrate how doping alters the electronic band structure of host transparent conductors, we calculated the band structure of undoped and 12.5% Sc-doped CdO using the full-potential linearized augmented plane-wave method [6] (FLAPW) within the screened-exchange LDA approach [7]. As one can see from fig. 1, the optical window broadens upon
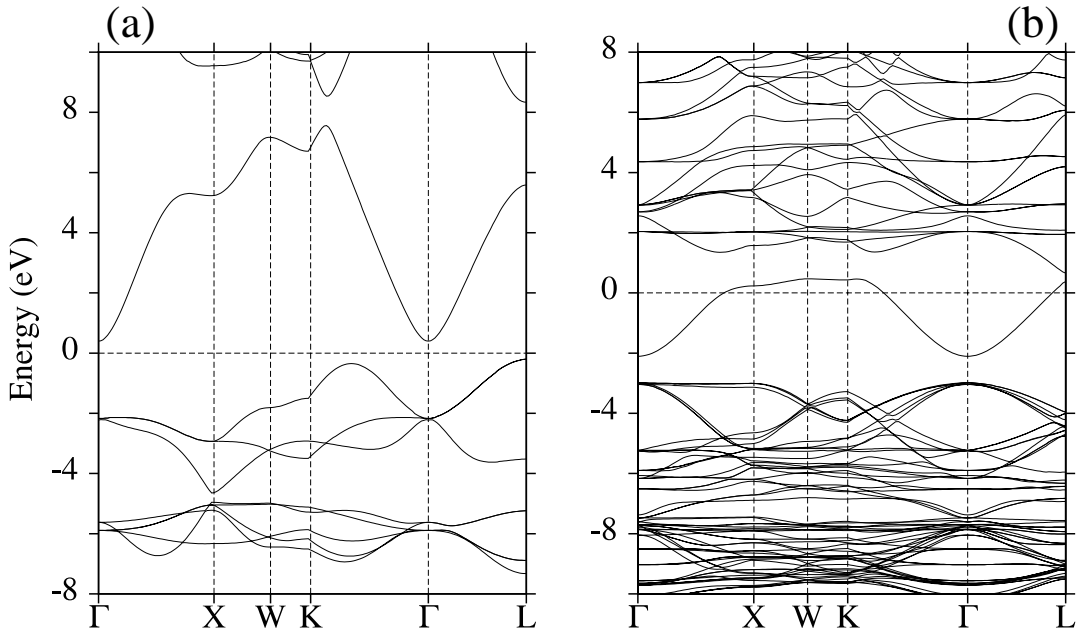
Fig. 1 – The electronic band structure of (a) undoped and (b) 12.5% Sc-doped CdO.

doping (Burstein-Moss shift) so that the intense interband transitions from the valence band are > 3.0 eV for the doped CdO. However, due to the interband transitions from the partially occupied band at the top of the conduction band, the complete, *i.e.*, 100% transparency in the visible range can never be achieved in the conventional TCOs. In addition, complex preparation methods are required to obtain practically useful combination of electrical conductivity and low absorption of visible light, since a decrease of the optical absorption comes at the cost of a greatly increased resistance: a lower dispersion of the single band which crosses the Fermi level would result in higher effective masses and hence in lower carrier mobility in doped CdO.

Recently, an insulator-conductor conversion was discovered in an oxide that differs essentially from the known TCO by its chemical and structural properties and by the origin of the induced conductivity: the cage structured insulating calcium-aluminum oxide, $12CaO \cdot 7Al_2O_3$, or mayenite, showed a persistent conductivity upon doping with hydrogen followed by ultraviolet irradiation [8]. First-principles electronic band structure calculations [9] have already revealed that the charge transport associated with the electrons excited off the hydrogen ions $(H^- \rightarrow H^0 + e^-)$ occurs by electron hopping through the encaged "defects" —the H^0 and OH^- located inside the large (more than 5.6 Å in diameter) structural cavities. The low conductivity of the material (~ 1 S/cm, refs. [8,9]) was attributed to the strong Coulomb interactions between the UV released electrons which migrate along a narrow conducting channel —the hopping path. Indeed, the alleviation of their electronic repulsion [10] resulted in the observed [11] 100-fold enhancement of the conductivity in the mayenite-based oxide, $[Ca_{12}Al_{14}O_{32}]^{2+}(2e^-)$, although the carrier concentration is only two times larger than that in the H-doped UV-irradiated $Ca_{12}Al_{14}O_{33}$. The improved conductivity, however, came at the cost of greatly increased absorption [10,11], making this oxide unsuitable for practical use as a transparent conducting material.

Despite the failure to combine effectively the low optical transparency and useful electri-
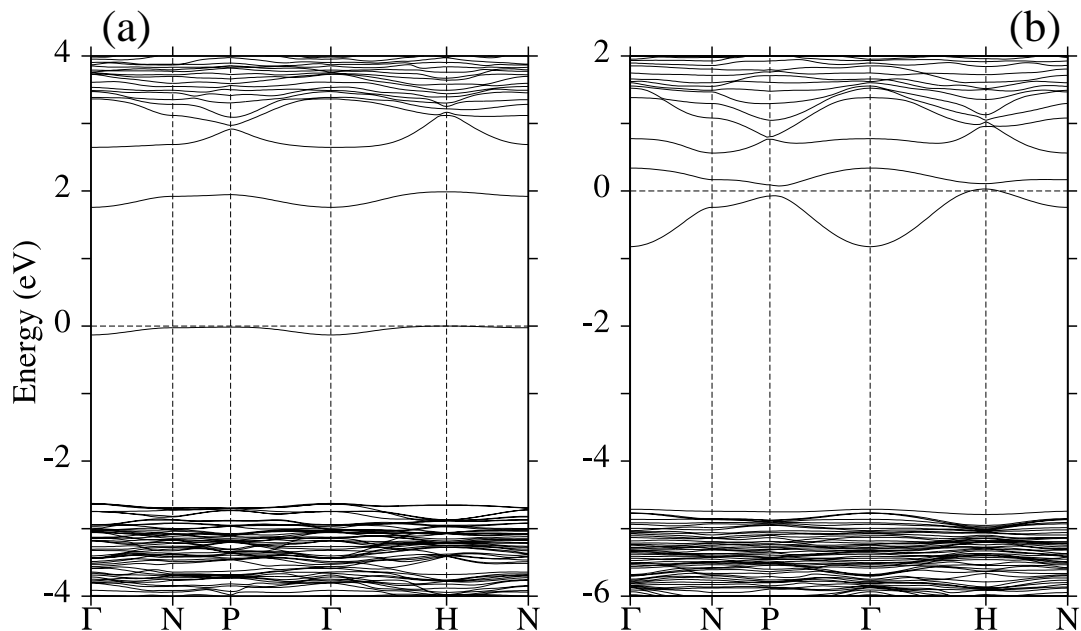
Fig. 2 – The electronic band structure of H-doped mayenite (a) before and (b) after UV-irradiation.

cal conductivity in the mayenite-based oxides, the nature of their electronic band structure suggests that these materials belong to a conceptually new class of TCOs. Using the linear muffin-tin orbital method in the atomic sphere approximation [12], we calculated the electronic band structure of the H-doped $12CaO \cdot 7Al_2O_3$ before and after UV-irradiation [13]. The results are presented in fig. 2. As one can see, hydrogen annealing and the subsequent UV-irradiation of $Ca_{12}Al_{14}O_{33}$ result in the formation of a *new* hybrid "defect" band in the band gap of insulating mayenite. This band crosses the Fermi level making the system conducting. Further, the transitions from the occupied part of the band to the unoccupied one are below the visible range due to the narrowness of the hybrid band (< 1.2 eV), while the interband transitions to the bottom of the conduction band are rather weak since they are provided by the low density of states (DOS) in the hybrid band near E_F. Consequently, any increase of the DOS at E_F that favors a higher conductivity, would result in an increase of light absorption, reducing the optical transmission. Indeed, this was observed [11] for $[Ca_{12}Al_{14}O_{32}]^{2+}(2e^-)$, where the DOS at E_F is found to be 24 times larger than in the H-doped UV-irradiated mayenite [10].

Thus, in striking contrast to the conventional TCOs, where the optical absorption cannot be eliminated for fundamental reasons (as discussed above), the band structure analysis of mayenite-based oxides suggests an approach to combine 100% optical transparency and high electrical conductivity. The schematic band structure of such an "ideal" TCO is shown in fig. 3. The introduction of a *deep* impurity band in the bandgap of an insulating material would help to keep intense interband transitions (from the valence band to the impurity band and from the impurity band to the conduction band) above the visible range. This requires the band gap of a host material to be more than 6.2 eV. Furthermore, the impurity band should be narrow enough (less than 1.8 eV) to keep intraband transitions (as well as the plasma frequency) below the visible range.

In order to achieve high conductivity, the concentration of impurities should be large enough so that their electronic wave functions overlap and form an impurity *band*. The
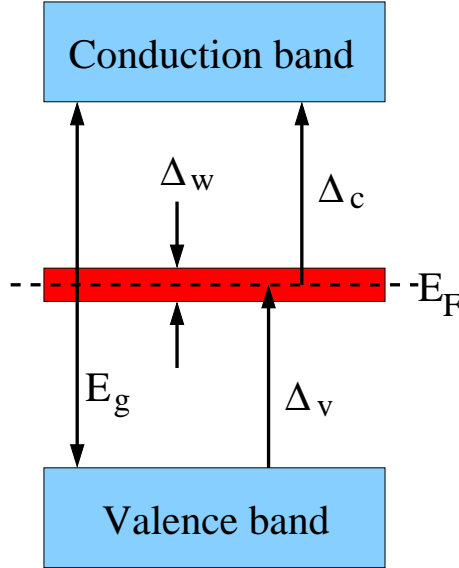
Fig. 3 – The schematic band structure of "ideal" TCO: $\Delta_w < 1.8\,\text{eV}$, $\Delta_v > 3.1\,\text{eV}$ and $\Delta_c > 3.1\,\text{eV}$ provide 100% transparency in the visible range.

formation of the band would lead to a high carrier mobility due to the extended nature of these states resulting in a relatively low scattering. For this, a material with a close-packed structure should *not* be used, because large concentration of impurities would result in i) an increase of ionized impurity scattering which limits electron transport [14,15]; and ii) a large relaxation of the host material, affecting its electronic structure and, most likely, decreasing the desired optical transparency. Therefore, an introduction of a deep impurity band into a wide-band insulator with a close-packed structure would make the material neither conducting nor transparent. In sharp contrast, nanoporous structure materials offer a way to incorporate a large concentration of impurities without any significant changes in the band structure of the host material, *e.g.*, H^- and OH^- in the spacious cages of mayenite.

In mayenite, however, the encaged impurities are well separated from each other and, therefore, do not form by themselves an impurity band that is necessary for creating extended well-conducting electronic states, cf. fig. 2(a). Although the applied UV-irradiation overcame this problem, cf. fig. 2(b), giving rise to a 10 orders of magnitude increase of the conductivity, it led to a degradation of the optical properties: since the new hybrid band was formed not only from states of the encaged impurities but also from states of atoms belonging to the cage wall (namely, $3d$ states of Ca atoms which form the bottom of the conduction band, ref. [9]), this band was effectively shifted towards the conduction band minimum.

Alternatively, the coupling between impurities can be achieved by choosing a material where an array of connected structural cavities (channels) will allow the interaction of the nearby impurities —unlike the mayenite-type materials where the encaged impurities are iso- lated. For this, novel materials called electrides [16] (in particular, inorganic electrides which

are alumino-silicate zeolites with dissolved alkali metals [17]) seem to be very promising candidates for "ideal" TCOs due to their unique structural, optical and electronic properties [18–21] —namely, intercavity channels [22], large bandgaps, weak binding of the "excess" electrons and near-metal electronic conductivity.

Finally, while the conductivity in the proposed new type of TCO materials may not exceed the maximum value of the conventional TCOs, *i.e.*, $\sim 10^4\,\mathrm{S/cm}$ (due to similar intrinsic limits [23–25]), their optical transparency can be expected to be as high as 100% in the visible wavelength range.

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REFERENCES

[1] Streintz F., *Ann. Phys. (Leipzig)*, **9** (1902) 854; Badeker K., *Ann. Phys. (Leipzig)*, **22** (1907) 749.
[2] Thomas G., *Nature*, **389** (1997) 907.
[3] Ginley D. S. and Bright C. (Editors), *Mater. Res. Bull.*, **25** (2000) 15, and articles therein.
[4] Stoute S., *Mater. World*, **11** (2003) 12.
[5] Mryasov O. N. and Freeman A. J., *Phys. Rev. B*, **64** (2001) 233111.
[6] Wimmer E., Krakauer H., Weinert M. and Freeman A. J., *Phys. Rev. B*, **24** (1981) 864.
[7] Asahi R., Mannstadt W. and Freeman A. J., *Phys. Rev. B*, **59** (1999) 7486.
[8] Hayashi K., Matsuishi S., Kamiya T., Hirano M. and Hosono H., *Nature*, **419** (2002) 462.
[9] Medvedeva J. E., Freeman A. J., Bertoni M. I. and Mason T. O., *Phys. Rev. Lett.*, **93** (2004) 016408.
[10] Medvedeva J. E. and Freeman A. J., *Appl. Phys. Lett.*, **85** (2004) 955.
[11] Matsuishi S., Toda Y., Miyakawa M., Hayashi K., Kamiya T., Hirano M., Tanaka I. and Hosono H., *Science*, **301** (2003) 626.
[12] Andersen O. K., Jepsen O. and Sob M., *Electronic Band Structure and its Applications*, edited by Yussouff M. (Springer-Verlag, Berlin) 1986.
[13] The calculations were performed for $12\mathrm{CaO} \cdot 7\mathrm{Al_2O_3}$ with one formula unit, *i.e.*, a total of 59 atoms per cell which combine into six cages; 85 empty spheres were included to fill out the open space.
[14] Brooks H., *Adv. Electron. Electron. Phys.*, **7** (1955) 85.
[15] Dingle R. B., *Philos. Mag.*, **46** (1955) 831.
[16] Dye J. L., *Science*, **247** (1990) 663; *Nature (London)*, **365** (1993) 10.
[17] Edwards P. P., Anderson P. A. and Thomas J. M., *Acc. Chem. Res.*, **29** (1996) 23.
[18] Dye J. L., *Inorg. Chem.*, **36** (1997) 3816.
[19] Singh D. J., Krakauer H., Haas C. and Pickett W. E., *Nature*, **365** (1993) 39.
[20] Petkov V., Billinge S. J. L., Vogt T., Ichimura A. S. and Dye J. L., *Phys. Rev. Lett.*, **89** (2002) 075502.
[21] Li Z., Yang J., Hou J. G. and Zhu Q., *J. Am. Chem. Soc.*, **125** (2003) 6050.
[22] The absence of an array of cavities or channels in mayenite is in accord with the finding that $[\mathrm{Ca_{12}Al_{14}O_{32}}]^{2+}(2\mathrm{e}^-)$ cannot be classified as an electride [10] as suggested originally [11].
[23] Bellingham J. R., Phillips W. A. and Adkins C. J., *J. Mater. Sci. Lett.*, **11** (1992) 263.
[24] Coutts T. J., Wu X., Mulligan W. P. and Webb J. M., *J. Electron. Mater.*, **25** (1996) 935.
[25] Robbins J. J. and Wolden C. A., *Appl. Phys. Lett.*, **83** (2003) 3933.