DOI: 10.1002/((please add manuscript number))

**Article type: Full Paper**

Chemical Control of Correlated Metals as Transparent Conductors

Jessica L. Stoner, Philip A. E. Murgatroyd, Marita O’Sullivan, Matthew S. Dyer, Troy D. Manning, John B. Claridge, Matthew J. Rosseinsky\* and Jonathan Alaria\*

Dr. M. O’Sullivan, Dr. T. D. Manning, Dr. M. S. Dyer, Dr. J. B. Claridge, Prof. M. J. Rosseinsky

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, United Kingdom

E-mail: m.j.rosseinsky@liverpool.ac.uk

J. L. Stoner, P. A. E. Murgatroyd, Dr. J. Alaria

Department of Physics, University of Liverpool, Oxford Street, Liverpool, L69 7ZE, United Kingdom

E-mail: jonathan.alaria@liverpool.ac.uk

Keywords: (correlated metals, optical properties, electrical properties, chemical control, transparent conductors)

Correlated metallic transition metal oxides offer a route to thin film transparent conductors that is distinct from the degenerate doping of broad band wide gap semiconductors. In a correlated metal transparent conductor, inter-electron repulsion shifts the plasma frequency out of the visible region to enhance optical transmission, while the high carrier density of a metal retains sufficient conductivity. By exploiting control of the filling, position and width of the bands derived from the B site transition metal in ABO3 perovskite oxide films, we show that pulsed laser deposition-grown films of cubic SrMoO3 and orthorhombic CaMoO3 based on the second transition series cation *4d2* Mo4+ have superior transparent conductor properties to the first transition series *3d1* V4+-based SrVO3. The increased carrier concentration offered by the greater bandfilling in the molybdates gives higher conductivity while retaining sufficient correlation to keep the plasma edge below the visible region. The reduced binding energy of the *n* = 4 frontier orbitals in the second transition series materials shifts the energies of oxide *2p* to metal *nd* transitions into the near-ultra violet to enhance visible transparency. The A site size-driven rotation of MoO6 octahedra in CaMoO3 optimizes the balance between plasma frequency and conductivity for transparent conductor performance.

1. Introduction

Transparent conducting materials have a wide variety of applications. They are a key component of photovoltaic and display technologies, and increasing demands are being made of such materials to continue the rapid growth of these industries.[1] Suitable TCMs are identified primarily via a high electrical conductivity and a small optical absorption in the visible part of the spectrum (1.75 – 3.2 eV). Transparent Conducting Oxides (TCOs) are the current front-running commercial materials with Tin-doped Indium Oxide (ITO) and Fluorine-doped Tin Oxide (FTO) being the most widely used.[2, 3] These compounds are wide band gap (> 3 eV ) semiconductor oxides with no intra-band transition in the visible spectrum, therefore offering high transparency. A high level of doping shifts the Fermi level into the conduction band to provide metallic-like electrical conduction, with the free carrier reflection edge (represented by the screened plasma energy *ωp*) below the near-infrared region of the spectrum (< 1.75 eV). In these classical degenerately-doped semiconductor TCOs, there is direct competition between *ωp* and the electrical conductivity *σ*, which are both controlled by the carrier density and effective mass but in antagonistic ways, as described in Equations 1 and 2, [3, 4]

(Equation 1)

where *q* is the electrical charge, *ε*0 the permittivity of space, *ε*r the relative permittivity of the compound, *neff* the effective carrier concentration and *m*\* the effective mass of the carrier, and

(Equation 2)

where τ is the scattering time of the carrier.

This competition governs the optimization of *neff* and *m*\* in wide band gap TCOs, where increase in carrier density and a reduction of effective mass is pursued to maximize conductivity, at the cost of increasing the plasma frequency while simultaneously reducing transparency in the visible. The overall performance of the TCO is quantified by the Haacke Figure Of Merit[5] (FOM), ,where *T* is the average transmittance in the visible and *Rs* is the sheet resistance. In practice, the maximum attainable conductivity in semiconductors is fundamentally limited, as increasing dopant concentration to raise the number of carriers decreases carrier mobility due to ionized impurity scattering and grain boundaries. [6] Other practical limitations of doped semiconductor TCOs include low solubility limit of the dopant, toxicity of common dopants such as fluorine in FTO (with the use of HF in the production process) and the scarcity of In increasing the cost of ITO. The current alternative to TCO materials is a very thin layer of a conventional metal such as Ag. In this case the overall performance of the material as a TCM is limited by the large electron mean free path of conventional metals (≈ 50 nm) increasing the interfacial scattering and therefore reducing the coating conductivity.

Recently, a new class of TCOs was introduced where the plasma frequency of a metal (SrVO3), rather than a semiconductor, is controlled by the correlations produced by the electron-electron interaction, which is comparable in size to the electronic bandwidth and thus significantly modifies transport and optical properties. In these correlated metallic oxides,[7] *m*\* in Equations 1 and 2 is replaced with the renormalized effective mass where is the free non-interacting electron effective mass and *Zk* is the renormalization factor produced by the electronic correlations. As illustrated in **Figure 1** (a), the coherent Drude-based plasma edge can be renormalized out of the visible range by these correlations. The resulting reduction of the conductivity due to the heavier electrons is compensated by the high carrier density of a metal and therefore less problematic for TCM performance than for a doped semiconductor. The additional benefit of the mass renormalization is that the electron mean free path in these correlated metals is shorter (< 10 nm) compared to conventional metals and therefore thin layers of materials can be deposited without reducing the conductivity.[7]

2. Concept

This new approach offers opportunities to control the performance of correlated metal TCOs. *ωp*(*Zk*,*neff*) calculated from equation 1 with *neff =* 2.2·1022 cm-3 observed for SrVO3 is shown in Figure 1(a) (solid green line), with the reported plasma frequency of 1.33 eV shown as a green circle at *Zk* = 0.33. The plasma frequency of SrVO3 lies below the 1.75 eV threshold, and the conductivity could therefore be increased (lower panel Figure 1 (a)) without compromizing optical performance if *ωp* was shifted towards this threshold, resulting in a reduced *Zk* = 0.58 for the same *neff*. This suggests that the correlation in SrVO3 may be too strong, and since there is no straightforward route to reducing the correlation strength in a given compound, alternative materials should be considered. Band filling is a materials design parameter that can be used to maximize the conductivity via the carrier density, as suggested by the *ωp*(*Zk*) calculated for the same as SrVO3, but using the theoretical *neff* = 3.18·1022 cm-3 of the *4d2* compound SrMoO3 (Figure 1 (a) purple curve and purple square). As expected *ωp* is shifted to higher energy and the 1.75 eV threshold is achieved for smaller *Zk*. The optimum *Zk* = 0.48 calculated for SrMoO3 is close to the value of ≈ 0.5 measured by photoemission and suggest that SrMoO3 could be under-correlated with the potential to increase the correlation using bandwidth control. [8]

In transition metal oxides, unlike post-transition metal closed shell-based semiconductors, such as doped ZnO, In2O3 and SnO2, the influence of the low-lying occupied transition metal *nd* states on the optical properties must be considered, in particular the Laporte-allowed O *2p* to metal *nd* charge-transfer inter-band transitions. We tackle this problem by controlling the B site transition metal frontier orbital energies and occupancies in the ABO3 perovskite. The selection of a *4d2* rather than a *3d1* system will have a beneficial impact on the inter-band transition energy through its influence of both band filling and band position, as illustrated in Figure 1(b). In SrVO3, where correlations shift the collective electron plasma response into the near infra-red, the main contribution to the remaining optical absorption in the visible is the high oscillator strength O *2p* - V *3d* charge transfer transition,[7] where electrons near the top of the O *2p* band occupy empty states above the Fermi energy *E*F in the 1/6 filled *t2g* band of *d1* SrVO3, as indicated by a black arrow in Figure 1 (b). *4d* orbital energies in the second transition series (purple arrow in Figure 1 (b)) are higher than those of the *3d* orbitals in the first series (green arrow in Figure 1 (b)) for reasons traceable to the electronic structure of the hydrogen atom, illustrated by the 10 eV reduction in the 5th ionisation energy in the gas phase from V to Mo. While this difference is of course reduced by Madelung site potential and orbital overlap effects in the solid state, ligand to metal charge transfer energies are expected to be higher in the second transition series than the first as a result. The combined effect of metal frontier orbital energies and band filling when replacing *3d1* V4+ with *4d2* Mo4+ can push these strong inter-band transitions above the visible range (black arrows on the right side of Figure 1 (b)).

The *4d* orbitals extend further beyond the core electrons than the *3d*, which increases the bandwidth through better orbital overlap and reduces interelectron repulsion, diminishing the role of correlation measured by *Zk*. If this decreases too far, the resulting under-correlated metals would have *ωp* in the visible, as illustrated by the purple star in Figure 1 (c). In contrast to SrVO3 where a lighter effective mass is required to reach the optimum plasma frequency, band narrowing driven by the size of the A site cation can be used to lower the effective mass of AMoO3 perovskites via MoO6 octahedral tilting to restore the optimal balance between *ωp* and σ. On substitution of A = Sr2+ with the smaller A = Ca2+, cubic SrMoO3 becomes orthorhombic CaMoO3 due to octahedral tilts which reduce the coordination number of Ca and the Mo-O-Mo bond angle below the ideal 180° by an angle *ϕ* (inset of Figure 1 (c)). This tilting distortion reduces the Mo *4d* - O *2p* overlap and increases the effective mass to , where *dMo-O* is the Mo-O interatomic distance. [9] This results in a lower plasma frequency as illustrated by the solid purple line in Figure 1 (c), which shows that for and *Zk* = 0.5, the plasma frequency would be at the edge of the visible, with the lowering of the conductivity from the reduced mobility outweighed by the enhanced transmission in the visible.

3. Electrical and optical properties of epitaxial SrMoO3 and CaMoO3 thin films

SrMoO3 is a cubic perovskite (inset of **Figure 2** (a)) and is one of the most conducting metallic oxides with a room temperature resistivity of 5.1 μΩ.cm . [10] Recent thin film studies have focused on its application for plasmonic [11] and microwave [12] technologies. To assess the influence of replacing *3d1* V4+ with *4d2* Mo4+ on the performance of correlated metal transparent conductors, we have grown SrMoO3 films with a thickness of 47 nm and RMS surface roughness of 0.3 nm (Supporting Information, Figure S1) and studied their electrical transport and optical properties which are compared with Density Functional Theory (DFT) calculations (Figure 2). Highly (0 0 L) oriented SrMoO3 have been obtained with a minor impurity (004) reflection from SrMoO4, which could be due to surface oxidation in the SrMoO3 sample(Figure 2 (a)), the lattice parameters for SrMoO3 were calculated from reciprocal space mapping (Supporting Information, Figure S2) and out-of-plane diffraction with *a* = 3.96(2) Å, *b* = 3.97(2) Å in-plane and *c* = 4.01(1) Å suggesting a small tetragonal distortion with *c*/*a* = 1.01. The in-plane lattice parameters are close to the reported value for bulk cubic SrMoO3 with *abulk* = 3.976 Å and a small tetragonal distortion is observed below 266 K in the bulk material. [13] Despite the relatively small lattice mismatch between SrMoO3 and SrTiO3 (-1.7%), the rocking curve presents a broad Gaussian (FWHM 0.92°) and narrow Lorentzian component (FWHM 0.065°) (inset of Figure 2 (a)), which indicate the presence of dislocations in the films. This is consistent with the higher room temperature resistivity of 18 μΩ.cm and lower Residual Resistivity Ratio (RRR) = *ρ*(300K)/*ρ*(4K) = 1.5 (Supplementary Information, Figure S3) compared to the RRR = 14 reported in single crystals.[10]

The temperature dependence of the resistivity of SrMoO3 is typical of a correlated metal where below a critical temperature *T*\* = 85 K (Figure 2 (b)), electron-electron scattering is the dominant mechanism presenting a *T*2 dependence. Above *T*\*, the temperature dependence of the resistivity begins to deviate from the *T*2 relationship and phonon scattering becomes important. The carrier concentration, *neff*, and mobility *µ*, as function of temperature are shown on Figure 2 (c). A carrier concentration of 3.15(7)·1022 cm-3 is found at 300K for SrMoO3 and remains constant within error down to 5 K, in good agreement with the theoretical carrier concentration of 3.18·1022 cm-3 calculated for *d2* SrMoO3. As expected from the band filling argument, this is higher than the theoretical value of 1.67·1022 cm-3 for *d1* SrVO3 and the reported value of 2.2·1022 cm-3 for *d1.2* SrVO2.90. [14] The carrier mobility for SrMoO3 is 11 cm2·V-1·s-1 at room temperature, corresponding to an average scattering time of 19 ps assuming an effective mass of 3 m0. These values are similar to the value reported for SrVO3, and confirms that the increased conductivity from 3.5·104 S/cm for SrVO3 to 5.6·104 S/cm in SrMoO3 is controlled by band filling. The mobility starts to increase at lower temperature to a maximum of 15 cm2·V-1·s-1 at 5K and a change of slope is observed at the same value as *T*\*, confirming the change of dominant scattering mechanism from electron-electron below *T*\* to phonon scattering above *T*\*. Ellipsometry measurements (Supplementary Information, Figure S4) were fitted with a combination of Drude and Lorentz oscillators (Supplementary Information, Table S1) to extract the complex dielectric function presented in Figure 2 (c). The reduced plasma energy *ωp*, defined as the energy at which the real part of the complex dielectric function *ε*1 is equal to zero, is measured as 1.73 eV (purple dashed-dotted line in the top panel of Figure 2 (c)), consistent with previous reports giving a value between 1.75 and 2.0 eV. [15, 16] This shift of the plasma frequency towards the visible compared to SrVO3 (arrow in top panel Figure 2 (c)) make SrMoO3 an ideal system to maximize the conductivity.

The other drastic change in the optical properties between the *3d1* and *4d2* compounds is the shift of the strongest inter-band transition features in *ε*2 (black arrow lower panel in Figure 2 (c)) from 3.02 eV in SrVO3 to 4.34eV, well above the highest visible energy of 3.25eV, thus offering an enhanced window of transparency in SrMoO3 (Supplementary Information, Figure S5). To confirm the origin of the shift of the inter-band transition, we compare the experimental dielectric constant to the DFT-calculated transition energies. The O *2p* - Mo *t2g* inter-band transitions for SrMoO3 were calculated from the dipole transition matrix elements and shown with blue circles on Figure 2(d), where the size represents the strength of the transition, with the strongest transitions and their energies indicated with arrows. The measured and calculated transition features of SrMoO3 are in excellent agreement, with a clear peak in *ε*2 at 4.37eV, matching that of the strongest calculated transition. The broadening of this peak corresponds to the second and third most intense transitions indicated in Figure 2 (d). This analysis shows that the enhanced band filling and higher orbital energy of the *t2g* bands, derived from a *4d2* rather than a *3d1* ion, increase *E*F and raise the charge transfer transition energies outside the visible region of the spectrum. Together with the increased conductivity, this leads to a Haacke FOM of 9.4·10-4 S for SrMoO3, which is fivefold higher than SrVO3 [7] and close to epitaxial ITO (1.0·10-3 S) [17] for an equivalent thickness.

To further optimize the performance of *4d*-based correlated transparent conductors, we investigate the chemical control of the optical and transport behaviour of AMoO3 phases via the Mo-O-Mo angle as proposed in Figure 1 (c) by studying the electrical and optical properties of a 57 nm epitaxial CaMoO3 thin film with a RMS roughness of 2.5 nm (Supplementary Information, Figure S6). The small size of the Ca2+ ions results in the tilting of the MoO6 octahedra lowering the symmetry of the bulk crystal structure to *a* *Pnma* orthorhombic cell with a pseudo-cubic lattice parameter of *ap.c.bulk* = 3.897 Å and a tilt angle ϕ ≈ 16.7 ° (inset of **Figure 3** (a)). [18] Using the pseudo-cubic lattice parameters, CaMoO3 has a lattice mismatch of 0.2 % with SrTiO3 and the out-of-plane Bragg film peaks are found to overlap with the substrate. The observation of Pendellösung fringes suggests a highly coherent film growth (Supplementary information, Figure S7) and the presence of half-order peaks in the pseudo-cubic setting specific to the orthorhombic distortion (Figure 3 (a)) confirms that the film have retained the bulk structure. The calculated orthorhombic cell parameters in the *Pnma* settings are *a* = 5.55 (2) Å, *b* = 7.81 (2) Å and *c* = 5.45(2) Å, corresponding to *ap.c.* = 3.89 (1) Å and a tilt angle ϕ ≈ 16.8 (5)°. The resistivity of CaMoO3 at 300 K is 67μΩcm with a RRR of 2.3 (Supplementary Information, Figure S8) which is slightly higher than in the SrMoO3 film. The temperature dependence of the resistivity (Figure 3(b)) exhibit a similar *T*2 behaviour at low temperature with a *T*\* = 120 K which is higher than in SrMoO3. The higher RRR and *T*\* suggest that the dislocation density in CaMoO3 films is lower than in SrMoO3 owing to the smaller lattice mismatch with SrTiO3. The room temperature carrier concentration is found to be 2.4(2)·1022 cm-3 which is lower than the theoretical value (3.4·1022 cm-3), and the temperature dependences of the carrier concentration and the mobility (Figure 3 (b)) do not follow the same trend as SrMoO3. The mobility presents a maximum at around *T*\* but, instead of saturating, decreases again on further cooling. Similarly the carrier concentration starts increasing around *T*\* and reaches 4.4(2)·1022 cm-3 at 5 K. These behaviors suggest that the correlation effects increase below *T*\* and further increase the narrowing of the band leading to an increased *neff* and decreased mobility. Ellipsometry spectra (Supplementary Information, Figure S9) were fitted with a combination of Drude and Lorentz oscillators (Supplementary Information, Table S2) to extract the complex dielectric function presented in Figure 3 (c). The reduced plasma energy for CaMoO3 is shifted to 1.3 eV compared to 1.73 eV for SrMoO3 (black arrow on the top panel of Figure 3 (c)), far below the visible region which begins at 1.75 eV. As for SrMoO3, the *4d2* parentage of the *t2g* band shifts the inter-band charge-transfer transitions out of the visible region as a broad peak at 4.25 eV. To verify that the shift in the plasma frequency is controlled by bandwidth tuning, the DFT-calculated density of states of CaMoO3 is compared to SrMoO3 (Figure 3 (d)). The *t2g* bandwidths for SrMoO3 and CaMoO3 are calculated as 3.62 eV and 3.18 eV respectively. The ratio = 0.75 is close to the ratio = 0.77

showing that the reduction of plasma frequency is not only due to the smaller carrier concentration, but also from the larger effective mass of CaMoO3, because the octahedral tilting reduces the Mo-O-Mo overlap compared to cubic SrMoO3. This gives a lower plasma frequency, which outweighs the associated reduction in mobility because of the retained high carrier density. The position of charge transfer band is retained from the band position and filling approach and is chemically optimized. The reduced *t2g* bandwidth raises the bottom of the band compared to the top of the O *2p* band, which consists in perovskites of M-O non-bonding O 2p states that are less affected by the tilting. This fine tuning of the electronic band structure gives a superior Haacke FOM to cubic SrMoO3. The orthorhombic CaMoO3 value of 9.8·10-4 S matches epitaxial ITO for equivalent thickness.

4. Conclusions

We have demonstrated that by using the three chemically controllable parameters of carrier density, orbital energy and bandwidth we can tune the charge transfer band position, plasma frequency and conductivity to optimize the transparent conductor performance of non-toxic, earth abundant Mo-based correlated metal perovskite oxides to match the best-in-class wide band gap semiconductors. These strategies open new paths to chemically control the performance of correlated transparent conductors.

5. Experimental Section

*Thin film deposition*: SrMoO3 and CaMoO3 films were deposited via pulsed laser deposition on SrTiO3 (001) substrates. Dense ceramic targets of SrMoO4 and CaMoO4 were prepared via conventional solid state synthesis. A reducing environment of 2.5% H2 in Ar was used at 0.3mTorr in order to reduce the Mo6+ oxidation state of the target to the Mo4+ state of the targeted perovskite phase as demonstrated in previous reports. [12, 16, 19]. A nominal substrate temperature of 650°C was used with a laser fluence of 1.3 J/cm2 at a rate of 1 Hz. Both films presented a metallic luster with a red and brown shade for the SrMoO3 and CaMoO3 films respectively.

*Structural characterization*: The quality of the films was assessed using X-ray diffraction using a Rigaku SmartLab diffractometer including out-of-plane large angle scans, reciprocal space mapping, reflectivity and rocking curve analysis. The surface morphology of the film was studied by atomic force microscopy with an Agilent 5600LS Microscope.

*Electrical properties*: Resistivity and Hall resistance as a function of temperature were collected from 300K to 5K in the Van der Pauw configuration using a Quantum Design Physical Property Measurement System. To extract the Hall resistance the magnetic field was varied from -14 T to 14 T and the antisymmetric part of the measured resistivity was calculated.

*Optical properties*: Ellipsometry in the UV-NIR range was performed using a J. A. Woollam M200UI with a wavelength range of 240 to 1700nm (0.73 - 5.14eV).

*Computational methods*:The plane-wave based density functional theory (DFT) calculations were carried out using the VASP package [20] with the projector augmented wave method[21] to treat core electrons. The *s* and *p* semi-core states were treated as valence states for all elements except for oxygen. A plane-wave cut-off energy of 550 eV was used throughout, with the PBE functional. [22] 32×32×32 *k*-point grids were used for cubic SrVO3 and SrMoO3, and a 23×16×23 k-point grid for the orthorhombic CaMoO3. Unit cell parameters and atomic positions were optimized until the magnitude of all forces fell below 0.001 eV/Å. The high-symmetry paths of k-points used for band structure plots were created using AFLOW. [23] Transition matrix elements and the frequency dependent dielectric constant were computed following exact diagonalization of all 80 bands, neglecting local field effects. [24]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

We thank EPSRC for funding under EP/N004884 and EP/P001513/1.

Received: ((will be filled in by the editorial staff))  
Revised: ((will be filled in by the editorial staff))  
Published online: ((will be filled in by the editorial staff))

**References**

[1] a) C. G. Granqvist, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1529; b) C. Hilsum, *Philos. Trans. Royal Soc. A* **2010**, *368*, 1027; c) R. A. Afre, N. Sharma, M. Sharon, M. Sharon, *Revi. Adv. Mater. Sci.* **2018**, *53*, 79.

[2] a) S. C. Dixon, D. O. Scanlon, C. J. Carmalt, I. P. Parkin, *J. Mater. Chem. C* **2016**, *4*, 6946; b) T. Minami, *Thin Solid Films* **2008**, *516*, 5822.

[3] H. Mizoguchi, P. M. Woodward, *Chem. Mater.* **2004**, *16*, 5233.

[4] a) P. P. Edwards, A. Porch, M. O. Jones, D. V. Morgan, R. M. Perks, *Dalton Trans.* **2004**, *19*, 2995; b) A. J. Freeman, K. R. Poeppelmeier, T. O. Mason, R. P. H. Chang, T. J. Marks, *MRS Bull.* **2000**, *25*, 45; c) J. Gao, K. Kempa, M. Giersig, E. M. Akinoglu, B. Han, R. Li, *Adv. Phys.* **2016**, *65*, 553.

[5] G. Haacke, *J. Appl. Phys.* **1976**, *47*, 4086.

[6] a) B. J. Ingram, M. I. Bertoni, K. R. Poeppelmeier, T. O. Mason, *Thin Solid Films* **2005**, *486*, 86; b) P. D. C. King, T. D. Veal, *J. Phys. Cond. Matter* **2011**, *23*, 334214; c) A. T. Vai, N. Rashidi, Y. Fang, V. L. Kuznetsov, P. P. Edwards, *J. Phys. Cond. Matter* **2016**, *28*, 224003.

[7] L. Zhang, Y. Zhou, L. Guo, W. Zhao, A. Barnes, H.-T. Zhang, C. Eaton, Y. Zheng, M. Brahlek, H. F. Haneef, N. J. Podraza, Moses H. W. Chan, V. Gopalan, K. M. Rabe, R. Engel-Herbert, *Nat. Mater.* **2015**, *15*, 204.

[8] H. Wadati, J. Mravlje, K. Yoshimatsu, H. Kumigashira, M. Oshima, T. Sugiyama, E. Ikenaga, A. Fujimori, A. Georges, A. Radetinac, K. S. Takahashi, M. Kawasaki, Y. Tokura, *Phys. Rev. B* **2014**, *90*, 205131.

[9] a) M. Imada, A. Fujimori, Y. Tokura, *Rev. Mod. Phys.* **1998**, *70*, 1039, b) M. Medarde, J. Mesot, P. Lacorre, S. Rosenkranz, P. Fischer, K. Gobrecht, *Phys. Rev.* *B* **1995,** *52*, 9248, c) E. J. Moon, R. Colby, Q. Wang, E. Karapetrova, C. M. Schlepütz, M. R. Fitzsimmons, S. J. May, Nat. Comm. **2014**, *5*,5710.

[10] I. Nagai, N. Shirakawa, S.-i. Ikeda, R. Iwasaki, H. Nishimura, M. Kosaka, *Appl. Phys. Lett.* **2005**, *87*, 024105.

[11] M. P. Wells, B. Zou, B. G. Doiron, R. Kilmurray, A. P. Mihai, R. F. M. Oulton, P. Gubeljak, K. L. Ormandy, G. Mallia, N. M. Harrison, L. F. Cohen, S. A. Maier, N. McN. Alford, P. K. Petrov, *Adv. Opt. Mater.* **2017**, *5*, 1700622.

[12] A. Radetinac, A. Mani, S. Melnyk, M. Nikfalazar, J. Ziegler, Y. Zheng, R. Jakoby, L. Alff, P. Komissinskiy, *Appl. Phys. Lett.* **2014**, *105*, 114108.

[13] R. B. Macquart, B. J. Kennedy, M. Avdeev, *J. Solid State Chem.* **2010**, *183*, 250.

[14] P. Dougier, J. C. C. Fan, J. B. Goodenough, *J. Solid State Chem.* **1975**, *14*, 247.

[15] H. Mizoguchi, N. Kitamura, K. Fukumi, T. Mihara, J. Nishii, M. Nakamura, N. Kikuchi, H. Hosono, H. Kawazoe, *J. Appl. Phys.* **2000**, *87*, 4617.

[16] A. Radetinac, J. Zimmermann, K. Hoyer, H. Zhang, P. Komissinskiy, L. Alff, *J. Appl. Phys.* **2016**, *119*, 055302.

[17] H. Ohta, M. Orita, M. Hirano, H. Hosono, *J. Appl. Phys.* **2002**, *91*, 3547.

[18] C. de la Calle, J. A. Alonso, M. García-Hernández, V. Pomjakushin, *J. Solid State Chem.* **2006**, *179*, 1636.

[19] R. Aldin, S. T. Kei, A. Lambert, K. Masashi, T. Yoshinori, *Appl. Phys. Express* **2010**, *3*, 073003.

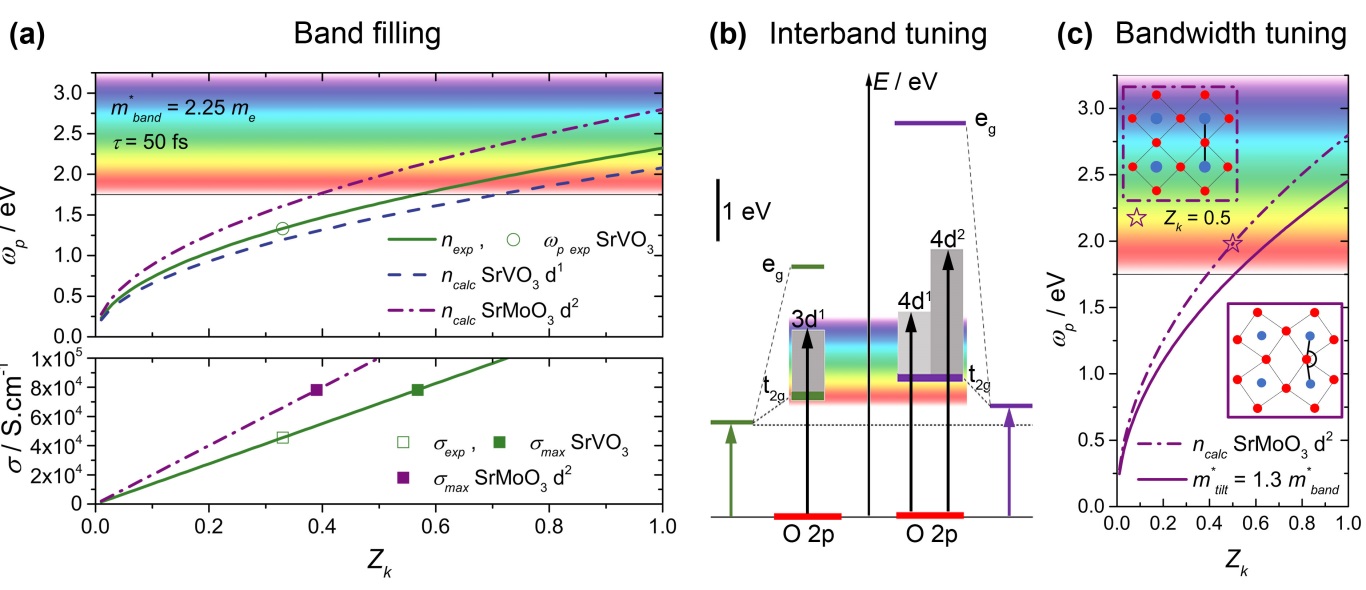
[20] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.

[21] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.

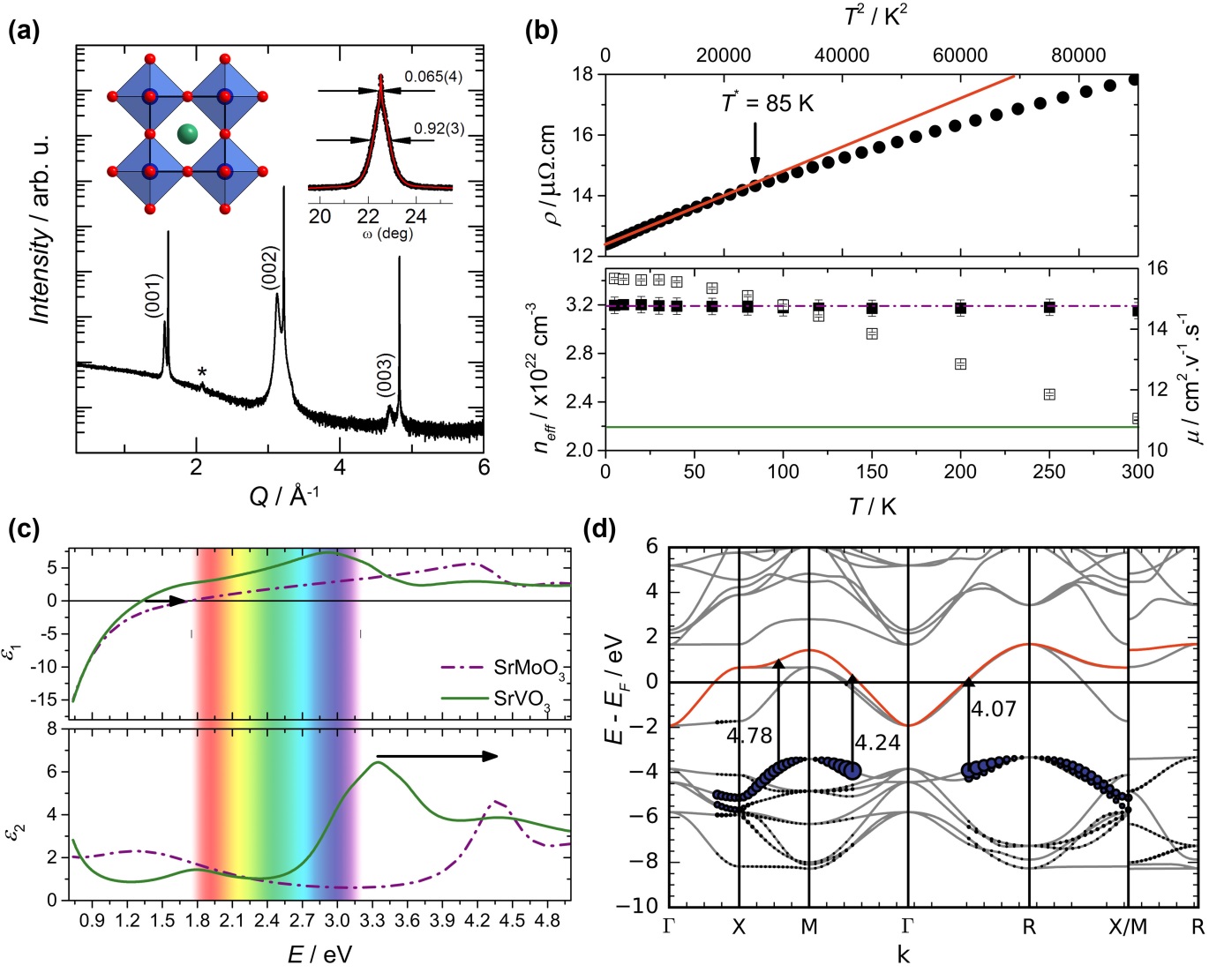
[22] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

[23] W. Setyawan, S. Curtarolo, *Comput. Mater. Sci.* **2010**, *49*, 299.

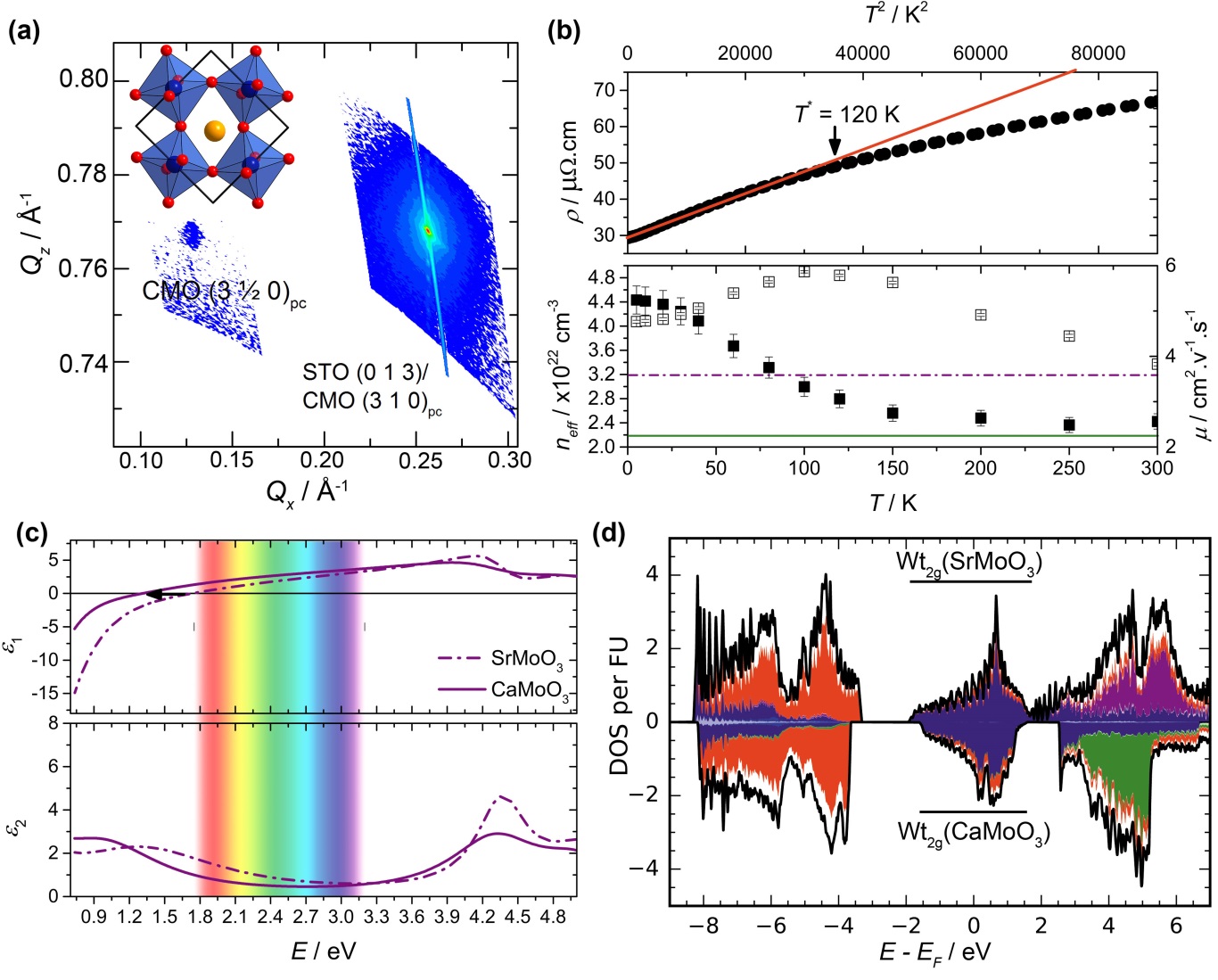
[24] M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, F. Bechstedt, *Phys. Rev. B* **2006**, *73*, 045112.



**Figure 1.** (a) Top panel: Calculated plasma frequency *ωp* as a function of the renormalization factor *Zk* using equation 1 with = 2.25 *me* for the theoretical (blue dashed line) and reported (solid green line) carrier concentration of *3d1* SrVO3 and for the theoretical carrier concentration of *4d2* SrMoO3 (purple dash-dot line). The experimental plasma frequency reported for SrVO3 with *Zk* = 0.33 is represented with an open green circle[7]. Bottom panel: Conductivity *σ* as a function of *Zk* calculated using Equation 2 with a scattering factor *τ* = 50 fs, to account for the measured mobility, and the reported carrier concentration of SrVO3 [7](solid green line) and for the theoretical carrier concentration of the *4d2* SrMoO3 (purple dash- dot line) together with the reported conductivity of SrVO3 [7](open green square) and the maximum theoretical conductivity corresponding to *ωp* = 1.75 eV for SrVO3 (full green square) and SrMoO3 (full purple square). (b) Schematic energy band diagram illustrating the O *2p* – *nd* inter-band transition for a *3d1* (left) and *4d1* and *4d2* cation (right) in an octahedral environment. (c) Calculated plasma frequency *ωp* as a function of the renormalization factor *Zk* using equation 1 with = 2.25 *me* for the theoretical carrier concentration of the *4d2* SrMoO3 (dashed dotted purple line) in a cubic structure (purple dash-dot border inset) and a tilted structure (purple border inset) with = 1.3 (purple line). The purple star represents *ωp* for *Zk* = 0.5 which was experimentally determined for SrMoO3 by photoemission and close to the optimum *Zk* to maximize the conductivity.[8]



**Figure 2.** (a) X-ray diffraction pattern of a 47 nm SrMoO3 thin film, the star corresponds to a minor SrMoO4 impurity phase. The rocking curve of the (0 0 2) reflection is shown in the right inset, and the cubic untilted structure of SrMoO3 in the left inset. (b) Top panel: resistivity as function of *T*2, the black dots are experimental data and the red line is a linear fit up to *T\**. Bottom panel: carrier concentration (black squares) and mobility (open squares) as function of T. The dash-dot purple line corresponds to the theoretical carrier concentration of SrMoO3 and the green line corresponds to the reported carrier concentration of SrVO3. [7] (c) Real part ε1 (top panel) and imaginary part ε2 (bottom panel) of the complex dielectric function spectra for SrMoO3 (purple dash-dot line) and SrVO3 (green line). (d) Computed transition matrix elements |*M*(*k*)|2 plotted as a function of *k* for transitions into *t*2g unoccupied bands from fully occupied states for SrMoO3. The red curve shows the unoccupied states, and the radius of the blue dots is proportional to the magnitude of |*M*(*k*)|2 for a transition from a particular occupied band at a given point in *k* space.

**Figure 3.** (a) Reciprocal space map of a 57 nm thick orthorhombic CaMoO3 thin film around the (3 1 0)p.c. and (3 ½ 0)p.c. reflections, indexed against the pseudocubic cell. The inset shows the tilted orthorhombic structure of CaMoO3. (b) Top panel: resistivity as function of *T*2, the black dots are experimental data and the red line is a linear fit up to *T\**. Bottom panel: carrier concentration (black squares) and mobility (open squares) as function of T. The dash-dot purple line corresponds to the theoretical carrier concentration of SrMoO3 and the green line the reported carrier concentration of SrVO3. [7] (c) Real part ε1 (top panel) and imaginary part ε2 (bottom panel) of the complex dielectric function spectra for CaMoO3 (purple line) and SrMoO3 (purple dash-dot line). The black arrow in the top panel indicates the decrease in plasma frequency from SrMoO3 to CaMoO3 (d) DFT calculated density of states (black lines) and site-projected density of states (Oxygen (red), Calcium (green), Molybdenum (blue) and Strontium (purple)) for SrMoO3 (top) and CaMoO3 (bottom).

**The chemical control of the electrical and optical properties of non-toxic, earth abundant Mo-based correlated metal perovskite oxides optimizes the transparent conductor performance to match the best-in-class wide band gap semiconductors.** The use of the three chemically controllable parameters (i) carrier density, (ii) orbital energy and (iii) bandwidth tune the charge transfer band position, plasma frequency and conductivity.

**Keyword**

**Correlated metals transparent conductor optimization**

J. L. Stoner, P. A. E. Murgatroyd, M. O’Sullivan, M. S. Dyer, T. D. Manning, J. B. Claridge, M. J. Rosseinsky\* and J. Alaria\*

Chemical Control of Correlated Metals as Transparent Conductors

ToC figure ((Please choose one size: 55 mm broad × 50 mm high **or** 110 mm broad × 20 mm high. Please do not use any other dimensions))

