A review on the p-type transparent Cu–Cr–O delafossite materials

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ABSTRACT

Transparent conductive oxides (TCOs) constitute a class of materials that combine high electrical conductivity and optical transparency. These features led to the development of the transparent electronics applications, such as flat panel displays, “smart” windows or functional glasses. *N*-type TCOs dominate the applications market, and the lack of a suitable *p*-type counterpart limits the fabrication of a completely transparent active device, which might be considered as a technological breakthrough. Among the wide range of *p*-type candidates, delafossite CuCrO₂ (and its out-of-stoichiometry derivatives) is a promising material to achieve the desired *p*-type TCO properties as, up to date, it is presenting the foremost trade-off between optical and electrical properties. The present paper covers the research work and the major achievements related to copper chromium delafossite. A comprehensive overview of fabrication methods and opto-electronic properties is presented. The source of doping and the charge carriers transport mechanism are also thoroughly discussed.

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GRAPHICAL ABSTRACT

Introduction

High electrical conductivity and wide band gaps—leading to high optical transparencies—are sought but seemingly mutually exclusive properties. In this context, the transparent conductive oxides (TCOs) are a special class of materials that combine both these properties. Depending on the donor (electrons) or acceptor (holes) level in the band gap of such materials, they are either *n*- or *p*-type, with carrier concentration (*n*, *p*) and optical band gap (E_g) typically around 10^{16} – 10^{21} cm⁻³ and 3 eV, respectively. The

most employed TCOs at industrial scale—Sn-doped In₂O₃ (ITO), Al-doped ZnO (AZO) and F-doped SnO₂ (FTO)—have *n*-type conductivity; among them, ITO stands out with electrical conductivity around 10³ S cm⁻¹ and transparency above 80% in the visible range [1, 2]. *N*-type TCOs have been reported and explored for more than half a century, and they dominate the transparent electronics market upon their two main applications: firstly, as transparent electrodes for flat panel displays and photovoltaic cells and secondly, as active layer for transparent thin film transistors (TFT), UV light-emitting diodes (LED), gas sensors or other transparent electronic

devices [3, 4]. However, challenges are still faced to find a matching p-type counterpart. (Extensive reviews can be found in [5–10].) The unveiling of a p-type material with similar properties would open a new era in transparent electronics, by promoting the fabrication of fully transparent active devices such as *p–n* junctions [6, 11], or complementary transistors [12–14]. This would open a new range of invisible electronics devices including smart windows [3, 15, 16], transparent UV LEDs [17, 18], solar-cell heterojunctions [19, 20], gas sensors [21–24], electromagnetic shielding [25], etc. Since the first report of a semitransparent p-type oxide, NiO [26], a large variety of materials has been investigated as a p-type TCOs suitable for applications:

- (i) Binary oxides: ZnO [9, 27–29], B₂O₃ [30], In₂O₃ [31], NiO [24, 26, 32, 33], SnO/SnO_x [34–37] and β-Ga₂O₃ [38–40].
- (ii) Mixed oxides: In₂O₃–Ag₂O [41, 42];
- (iii) Chromium based oxides: LaCrO₃ [43], Cr₂O₃ [44, 45];
- (iv) Ag-, Cu-, Pd- and Pt-based delafossites [46–56];
- (v) Layered oxychalcogenides: LaCuOS [57–59] and LaCuOSe [60];
- (vi) Spinel oxides: NiCo₂O₄ [61, 62], ZnCo₂O₄ [63, 64], ZnIr₂O₄ [63] and ZnRh₂O₄ [65, 66], etc.;
- (vii) Others: SnSeO [67], Ba₂BiTaO₆ [68], SrCu₂O₂ [69–71], [Cu₂S₂][Sr₃Sc₂O₅] [72] or La_{2/3}Sr_{1/3}VO₃ [73].

From a general point of view, these materials have failed to fully comply with the requirements of a p-type TCO for application purposes as they demonstrate either low conductivity or low transparency. The electrical conductivity (σ) of a material is directly proportional to the carrier concentration ($n_{e,h}$) and carrier mobility ($\mu_{e,h}$) with the last term depending on the carrier scattering relaxation time (τ) and the effective mass ($m_{e,h}^*$) of the carriers [74]:

$$\sigma = n_{e,h} \mu_{e,h} e = \frac{n_{e,h} e^2 \tau}{m_{e,h}^*} \quad (1)$$

Higher conductivities can be obtained by simply increasing n and/or the electrical mobility μ . For example, in n-type TCOs, the oxygen vacancies constitute one of the main defects inducing high carrier concentrations. The hybridization of s-orbitals—that

compose mainly the conduction band minimum (CBM)—with heavy-metal cations leads to a high level of delocalization and hence to low electron effective mass and high electrical mobility [75–77]. Recently, Fleischer et al. [7] presented a thorough report on the actual p-type TCOs performances. In a thought-provoking approach, they have analysed the changes on opto-electronic properties with the temperature of synthesis (Fig. 1), an important parameter when technological applications are envisaged.

An important conclusion might be drawn from their data: a TCO with high electrical conductivity and optical transparency is very difficult to be synthesized at low cost and always a trade-off between all these requirements must be foreseen. The challenge in improving optoelectronic properties of these p-type TCOs arises from their intrinsic electronic structure. The valence band edge of most oxide materials is composed by strongly localized oxygen 2p levels, owing to its large electronegativity [9]. These levels lie far lower than the valence orbital of the metallic atoms, leading to a non-dispersive valence band maximum (VBM). The high-electronegative oxygen atoms trap the holes, impeding therefore the introduction of shallow acceptors and inducing high effective hole mass, which leads to poor transport characteristics [9, 78]. Few aspects must be considered to favour a considerable hole

Figure 1 Comparison of the literature data of average transmission and sheet resistance of a spectrum of p-type transparent conducting oxides. The radius of the circles is inversely proportional to the temperature of the deposition process. Reprinted from Fleischer et al. [7]. Copyright [2017] MDPI Materials. Open Access.

concentration in a p-type semiconductor when doping is based on point or extended defects engineering [8, 79, 80]:

- (i) a low formation energy of point/extended defects that produce holes (e.g. native acceptors such as cation vacancies or oxygen interstitials);
- (ii) small ionization energy of these defects in order to release holes (i.e. a shallow acceptor level with respect to the host valence band);
- (iii) very important and valid also whatever the doping strategy, a high formation energy of native defects that annihilate holes (e.g. native donors such as anion vacancies).

Amidst *p*-type semiconducting materials, those having a delafossite structure were thoroughly investigated due to their interesting properties with applications in various fields. They are usually ternary metal oxides, with an AMO_2 -layered structure, where A^+ and M^{3+} are monovalent and trivalent cations, respectively. The A^+ cations have small size, favouring a linear coordination (two oxygen atoms); M^{3+} cations have coordination VI (six oxygen atoms), whilst the oxygen has coordination IV (one A^+ and three M^{3+}). Their structure comprises alternating close-packed layers of slightly distorted edge-shared M^{3+}O_6 octahedra, sandwiching planes of close-packed A^+ cations. The A^+ –O twofold coordination induces a dumbbell-shaped structure O–A–O unit placed parallel to the *c*-axis that connects to the adjacent M^{3+}O_6 octahedra [81–84]. Each O from the dumbbell is also coordinated to three M^{3+} cations, oriented in such form that the M^{3+}O_6 octahedron forms MO_2 layers parallel to the *ab* plane [5]. Delafossite materials can be thus considered natural nanolaminates with a panoply of design possibilities, according to the choice of A^+ and M^{3+} cations [85]. They can be divided into two groups, depending on the electronic configuration of A^+ cation (a noble metal from group X or XI), characterized by a closed-shell energy level close to (just above) the O^{2p} level [86–88]:

- (i) i) d^{10} ions (Cu^+ and Ag^+) [85, 89, 90]: usually present semiconducting or insulating behaviour and they are convenient for enhanced optical transparency.
- (ii) ii) d^9 ions (Pd^+ and Pt^+ [91–94]): In these materials, an unusual oxidation state is

stabilized by a metal–metal bonding [89]. Although these materials are metallic and opaque, ultrathin films have reasonably low sheet resistance and high transmittance, particularly in the near IR region.

Materials with delafossite structure have been known for more than 140 years; the first one, CuFeO_2 , was reported by Friedel in 1873 and named in honour of the French mineralogist and crystallographer Gabriel Delafosse. Yet, they became a subject to extensive interest after the 1997 report of Kawazoe and co-workers that successfully fabricated a stable *p*-type undoped CuAlO_2 with a considerable *p*-type conductivity ($\approx 1 \text{ S cm}^{-1}$) at that time [49]. They proposed a strategy—the so-called chemical modulation of the valence band (CMVB)—for broadening the valence band and consequently achieve lighter effective mass/higher carriers' mobility [71, 95]. Within this approach, they outlined three criteria that must be met in order to manipulate the valence band edge of *p*-type TCOs without compromising their optical transparency. Firstly, the *nd* energy levels of the shell of metallic cations and of O^{2p} should be similar to promote hybridization, hence forming strong covalent bonds. This leads to a more dispersive valence band edge pushed up above the bonding O^{2p} or metallic cations *nd* states. That furthermore ameliorates holes delocalization and consequently increases the carrier's. Mobility. Secondly, these levels should have closed electronic shells (nd^{10}) to avoid any coloration due by *d*–*d* excitations. Additionally, the coordination around oxygen atoms should be tetrahedral, allowing to pair the electrons from 2 *s* and 2 *p* orbitals of oxygen to bond with two other atoms. This configuration reduces the strong localization of the carriers at the VBM and removes the non-bonding nature of the O anions [8, 49]. From the theoretical point of view, the achievement of a *p*-TCO with improved characteristics relies on the delocalization of the VB by promoting the orbital hybridization between nd^{10} metal cations and O^{2p} orbitals. Figure 2 depicts a survey over the reports of electrical conductivity for Ag/Cu/Pd/Pt-based delafossite materials. A more comprehensive datasheet is presented in Table S I (Supplementary Information section). The values span a wide range of approximately eight orders of magnitude. Even in the case of the same material, the reported values vary due to the different method of

Figure 2 The highest reported values of electrical conductivity (measured at room temperature) for different doped and non-doped delafossite materials. A comprehensive survey is presented in Supplementary Information section (Table S.I).

synthesis or to the various approaches of tailoring the material. The highest values (with records beyond of $100\,000\text{ S cm}^{-1}$) are reported for the Pd/Pt delafossite [53, 56, 96, 97] but, as mentioned before, these ones show *typically* high reflectivity (optical metallic behaviour). Nonetheless, the ultrathin films demonstrate concomitant high values of electrical conductivity (even at critical thickness) and optical transmittance, making these materials very promising candidates for transparent electrodes [93]. Ag-based delafossites are expected to have wider band gap and lower visible-light absorption, due to the shift in the VBM to lower energies from Ag^{4d} states. Unfortunately, these delafossites have never been successfully synthesized in open systems due to the low free energy formation of Ag_2O ($-2.6\text{ kcal mol}^{-1}$) [98], which decompose to metallic Ag and O at $300\text{ }^\circ\text{C}$ before the reaction occurs [55, 88, 90]. Successful deposition methods usually require ion-exchange synthesis rather than a simple solid-state reaction [54] (hydrothermal synthesis in sealed autoclaves [98, 99], metathetical cation exchange [100] and oxidizing flux [101]), but low electrical conductivities have been achieved until now [51, 99, 102]. Nagarajan reported various Ag-based delafossites (doped and non-doped) in powder form, but only with very low conductivities around 10^{-4} – 10^{-6} S cm^{-1} [89]. Research is still under development for Ag-based delafossites to meet the requirements of optoelectronic applications; for instance, Wei [55] reported a facile chemical solution synthesis in an open

condition (spin coating + annealing) of 12% Mg-doped AgCrO_2 , obtaining a conductivity of $6.77 \times 10^{-3}\text{ S cm}^{-1}$.

Cu-based delafossites have attracted attention due to their expected large hole mobility, a result of the mixing of Cu^{3d} and O^{2p} states forming the valence band. It has been reported that this delafossite structure allows the hosting of a multitude of M cations, namely p-block elements (Al [49, 103, 104], B [105–107], Ga [54, 108, 109] or In [110–113]), transition metals (Co [114, 115], Cr [82, 116, 117], Fe [118–120], Mn [121, 122], Rh [123], Sc [124–126] and Y [89, 126–128]), or lanthanides (La [129–131], Nd [132], Pr [133], Sm and Eu [134]). These materials were thoroughly investigated as they demonstrated interesting properties in the different fields: antibacterial [135, 136], batteries [137], (photo)catalyse [83, 131, 138–140], luminescence [130], magnetic [141–145], ferroelectric [146], optoelectronics (most of the references of this article), supercapacitors [114], superconductors [147, 148] and thermoelectric [142, 149, 150].

Among Cu delafossites, the copper chromium oxide (CuCrO_2) is considered the most promising, as it presents a favourable covalent mixing between Cr^{3+} and O^{2-} , a high density of Cr^{3d} states near the VBM and a high band gap. Additionally, its optoelectrical properties are easy tuneable as the structure allows facile substitution with aliovalent and/or isovalent cations at the Cr site [81, 82, 151, 152]. Finally, it has a low synthesis temperature and a favourable thermal stability in air. To date, the highest conductivity reported values for this material are 278 S cm^{-1} for Mg and N co-doped CuCrO_2 using solid-state reaction, with a transmittance of 69% over the visible range [47] and 220 S cm^{-1} for a Mg/ CuCrO_2 with a transmittance around 30%, deposited by sputtering [117]. In the following, the present work will focus on synthesis and characterization of Cu–Cr–O delafossites. This review aims to give an overview of the studies on this material delafossites and of the most important reported results.

Structure of CuCrO_2 delafossite

The CuCrO_2 delafossite structure is composed of two alternating layers: a close-packed layer of slightly distorted edge-shared CrO_6 octahedra sandwiching planes of close-packed Cu cations, in dumbbell-

shaped linear coordination to oxygen anions in the adjacent CrO_6 layers [82, 83]. The Cr cation is located in the centre of the distorted edge-shared CrO_6 , and it has a + 3 oxidation state. The oxygen ion is in pseudo-tetrahedral coordination with one Cu and three Cr cations. In a simpler way, the delafossite structure can be visualized as consisting of two alternating layers: a planar layer of Cu cations in a triangular pattern and a layer of edge-sharing CrO_6 octahedra flattened with respect to the c-axis. Depending on the orientation of each layer in the stacking, CuCrO_2 has two polytypes (Fig. 3): ABA-BAB stacking leads to hexagonal α -2H polymorph (P63/mmc) [ICDD PDF 04-010-3329], whereas ABCABC leads to the rhombohedral α -3R polymorph (R-3 m) [ICDD PDF 04-010-3330]. In the primitive rhombohedral cell, there are four atoms: one Cu, one Cr and two O atoms [154, 155]. Among the Cu-based delafossites, the CuCrO_2 has relatively small a- and c-axes. However, the multitude of deposition or calculation techniques leads to an important span of values for lattice parameters. Table 1 depicts the values for the lattice parameters and the volume of unit cell from various experimental or theoretical works.

The calculated Cu–O and Cr–O bond lengths are 0.1881 nm and 0.1972 nm, respectively, in a good agreement with the values resulting from the Shannon atomic radii ($^{\text{II}}\text{O}^{2-} = 0.138 \text{ nm}$, $^{\text{II}}\text{Cu}^{1+} = 0.046 \text{ nm}$, $^{\text{VI}}\text{Cr}^{3+} = 0.062 \text{ nm}$ [156]). Significant deviations are then reported in the case of doped films. The size of the dopant (intrinsic or extrinsic) alters the normal inter-atomic distances. For example, in the case of Sc/ CuCrO_2 [157] the diffraction peaks shift to lower values of two-theta diffraction angles, in good

correlation with the radius of the substituting cation. For the doped sample, the “a” parameter is mainly affected, whilst the “c” one, related to the Cu–O distance, remains more or less unaltered. A different behaviour was reported in the case of delafossite films with an important deficit of Cu atoms. (33% of them are missing) A significant increase of c parameter was reported, more probably due to the increase of Cu–O averaged distance [161]. Within all crystallographic data reported for the Cu–Cr–O thin films, the very important aspect of thermal expansion is often neglected. The films are deposited on various substrates at temperatures up to 800 °C, and then, the XRD analysis is generally performed at room temperature. During the deposition process, the substrate is thermally expanded. The coefficient of thermal expansion for the most reported substrates is $0.54 \mu\text{K}^{-1}$ for Quartz and $7.54 \mu\text{K}^{-1}$ for sapphire, an order of magnitude difference. During the cooling process, the substrate is coming back to a non-deformed state, forcing the much thinner delafossite layer to contract also. Hence, for thin films below the critical thickness (above which typically the material is relaxed), the XRD analysis performed at room temperatures are mostly characterizing strained delafossite structures. A negative expansion coefficient [162–164] reported sometimes in the case of delafossites layers might complicate more the estimation of the actual strain induced. This is a very important aspect, as the induced strain changes the energetic band structure of the material and hence the optoelectronic behaviour might be severely affected [165–167].

The band structure of CuCrO_2 was theoretically determined using various approaches. The typical ones are: density functional theory (DFT) with a

Figure 3 Unit cells and $2 \times 2 \times 1$ stacks for CuCrO_2 . **a** Hexagonal α -2H polymorph (P63/mmc); **b** rhombohedral α -3R polymorph (R-3 m). Figures generated using VESTA software [153].

Table 1 Literature reports for CuCrO₂ lattice's parameters and the volume of unit cell. Adapted from [48] and revised

a (Å)	c (Å)	V (Å ³)	System	Exp/Theory	References
2.9748(1)	17.1016(5)	131.06	Rhombohedral	Experimental	[149]
2.9734(3)	17.100(4)	130.9	Rhombohedral	Theoretical	[155]
2.975	17.10		Rhombohedral	Experimental	[158]
2.962	17.01	129.24	Rhombohedral	Experimental	[159]
3.050	17.09		Rhombohedral	Theoretical	[158]
2.9740(3)	11.400(1)	87.32	Hexagonal	Theoretical	[154]
2.970	11.40	87.09	Hexagonal	Experimental	[160]
3.01–3.05	11.40–10.47	89.73–92.25	Hexagonal	Theoretical	[82]
2.97	17.24		Rhombohedral	Experimental	[161]

screened exchange local density approximation (sX-LDA) [168], the screened hybrid functional approach of Heyd, Scuseria and Ernzerhof (HSE06) [82], the generalized gradient approach (GGA) of Perdew, Burke and Ernzerhof (PBE) corrected for on-site Coulomb interactions (PBE + U) [82], the LDA + U approach [152] or many-body perturbation theory with the Green functions correlated with Coulomb interactions (GW approximation) [169]. In general, all these methods estimate a direct band gap between 2 and 4 eV and an indirect one between 1 and 3 eV. A summary of results is presented in Table 2. This relatively large dispersion of values is a result of the multitude of different assumptions, specific for each theoretical method. All approaches have their own advantages or disadvantages, offering good estimation for some parameters but getting loose for the others. For example, it is known the PBE overestimates the lattice parameters and underestimates the self-interaction, whilst HSE06 consistently produces structural data and band gap descriptions that are more accurate than LDA/GGA [82]. When

comparing these theoretical estimations with the reported experimental values (Fig. 5 within the paragraph dedicated to optical properties), the most precise approach seems to be the sX-

LDA or PBE + U approach. However, the theoretical models deal in general with bulk materials, with a well-defined crystalline structure, whilst the deposited films often present random defects, impossible to be accurately modeled. When the total electronic density of states is investigated, the delafossite CuCrO₂ presents few distinct regions (Fig. 4; from [82]). The levels below −4 eV are mainly broad and intense O^{2p} states, followed by narrow but also intense Cu^{3d} non-bonding states around −2 eV. These states are energetically degenerated with the weakly dispersive states from the non-bonding states of O^{2p} orbitals (at −2 eV). Finally, the bonding Cu^{3d} and O^{2p} states interact together and push up a mixed Cu–O state above the undispersed background at the VBM. This distribution was confirmed by X-ray resonant photoemission and X-ray absorption spectroscopy experiments of Yokobori [152] and Arnold

Table 2 Values of direct and indirect band gaps of CuCrO₂, as calculated by different theoretical approaches

Method	Direct band gap (eV)	Indirect band gap (eV)	Refs.
GGA	1.97	1.12	[168]
sX-LDA	3.1	2.9	[168]
PBE	—	1.06	[82]
PBE + U	—	2.06	[82]
HSE06	—	3.09	[82]
GGA	—	2.14	[170]
PBE	1.8284	1.065	[171]
PBE + U	2.3869	1.7083	[171]
PBE	1.3	0.96	[169]
GW	3.42	3.29	[169]
GW	3.42	3.42	[172]
GGA + U	2.55	2.04	[116]
PBE + U	1.72	1.67	[173]

Figure 4 The electronic density of states for CuCrO_2 . **a** Total EDOS; **b** Cu PEDOS; **c** Cr PEDOS (magnified 2x); **d** O PEDOS (magnified 2x). The blue lines represent d states, green s states and red p states. Adapted from Scanlon et al. [82] with the permission. Copyright (2010), AIP Publishing.

[116]. Both oxidation states of copper (+ 1 and + 2) were simultaneously observed in these experiments focused on.

Mg-doped CuCrO_2 . Finally, the Cr^{3d} states contribute mainly to the CBM. A minor contribution to VBM is also expected because of the bonds between three Cr ions and one O ion which produce hybridized Cr–O bonds [81].

Deposition methods

Various methods were reported to synthesize delafossite CuCrO_2 thin films, each of them leading to different morphological and optoelectronic properties. The majority of the reported fabrication techniques involves wet chemistry routes. Within this category, the most used seems to be the solid-state synthesis [47, 116, 143, 157, 174–177]. This consists in the mixing of $\text{Cu}_2\text{O}/\text{CuO}$ and Cr_2O_3 powders followed by high-temperature sintering and post-

treatments under different atmospheres. The CuCrO_2 is forming at temperatures higher than 800 °C under air and nitrogen atmosphere [158]. A special attention must be given in this case to avoid the formation of parasitic spinel CuCr_2O_4 phase that occurs at 500–700 °C. Under pure nitrogen atmosphere, the CuCrO_2 results from the direct reaction between Cu_2O and Cr_2O_3 around 700 °C. Usually, the solid-state processes take long time in order to remove moisture or any other organic impurity and for achieving good crystalline quality. In order to accelerate the synthesis, Kumar et al. use the microwave heating, as it enhances solid-state reaction kinetics [178]. Another chemical method of fabrication for copper chromium delafossite is the sol-gel process [179–186]. Copper and chromium hydrate precursors are dissolved in alcoholic or water-based solutions. For example, Wang [187] and Li [188] use copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) and chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) for fabricating CuCrO_2 thin films or targets for physical vapour depositions. Ngo [189] uses the same precursors but dissolved in distilled water with NaOH as the mineralizer and citric acid as a chelating agent. The last method using a chemical route is the hydrothermal synthesis, one of the most commonly used for preparation of nanomaterials [21, 190–193]. In this case, the chemical formation occurs in a wide temperature range from room temperature to very high temperatures, typically above 800 °C. Low- or high-pressure conditions can be used, depending on the vapour pressure of the main composition in the reaction. Gil [194] uses copper nitrate hemipentahydrate $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and chromium(III) nitrate nonahydrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in deionized water and NaOH solution. Ngo [189] used $\text{Cr}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ dissolved in water and Cu_2O dissolved in 3 M NaOH solution. However, the peculiar conditions (high temperatures or pressures) required by these methods exclude the direct use for the fabrication of transparent electronic devices and hence they are typically used for the synthesis of targets for the physical deposition processes (pulsed laser deposition or sputtering) methods. These methods also allow the fabrication of doped delafossite. The typical final product has a powder form, and the spin coating is furthermore used for thin films deposition. However, this is not adequate for large scale deposition, due to a poor long-range uniformity or control of the process [195].

A second category of deposition methods refers to physical vapour deposition (PVD) mainly the sputtering [47, 117, 196–203] and pulsed laser deposition [47, 145, 188, 204–208]. Vacuum-based techniques are preferred as this addresses the issue of the instability of Cu^+ and its sensibility to the oxygen partial pressure [209]. The PLD and some sputtering processes are used just as a material transfer method. A composite CuCrO_2 pellet fabricated using a method described above is used as target, and no other chemical compounds are involved. Laser or plasma is used to extract the material from this target and deposited in thin films forms. During the deposition, the substrate is usually heated at temperatures between 450 and 750 °C, with a crystalline delafossite phase observed usually this for temperatures higher than 500 °C [184, 199, 200, 202]. The films deposited using technique are smoother and more compact than those fabricated using the wet chemistry. This approach is often used when the synthesis of doped thin films is envisaged. A target already prepared with the intended stoichiometry is used in this case [117, 188, 206]. The involving of nitrogen gas during the deposition process leads to a N_2 -doped films with higher electric conductivity [47, 210]. Sun et al. [211] used also the DC co-sputtering (Cr and Cu targets) with oxygen as reactive gas. The films deposited in this case were amorphous and showed high resistivity. Very frequent, high-temperature annealing post-treatments under different atmospheres are engaged in order to fully convert the parasitic phases (CuO and CuCr_2O_4) to the CuCrO_2 phase or to engineer the thin films' morphology, strongly related to the optical properties. It is worth mentioning here the work of Shin [212] reporting the growth of CuCrO_2 thin films using the molecular beam epitaxy. This peculiar technique, despite its high energetic costs, is known to yield epitaxial thin films with almost no defects. The films deposited at a pressure of 5×10^{-10} mbar on Al_2O_3 (001) substrates showed (001) or (005) crystallographic orientations for temperatures of 700 and 800 °C, respectively.

The last category of methods for depositing the CuCrO_2 refers to chemical vapour deposition (CVD). Vapour of Cu and Cr (and dopant if required) precursors is sent in the reactor where they decompose and further react with Oxygen. Copper and chromium metallo-organic precursors such as acetylacetonates ($\text{Cu}(\text{acac})_2\text{-Cu}_{10}\text{H}_{14}\text{O}_4$, $\text{Cr}(\text{acac})_3\text{-Cr}_{15}\text{H}_{21}\text{O}_6$) or tetramethyl-heptadionates ($\text{Cu}(\text{thd})_2\text{-}$

$\text{C}_{22}\text{H}_{38}\text{CuO}_4$, $\text{Cr}(\text{thd})_3\text{-C}_{33}\text{H}_{57}\text{CrO}_6$) in solution are generally used [11, 48, 161, 213–216]. The use of these precursors prevents the alteration of electronic properties due to the absence of halide ions on the substrate [217]. The reaction takes place within the volume of the reactor CVD [215, 218]) or on the substrate surface (atomic layer deposition (ALD) [219]). The main advantage of these methods consists of the high conformality of the deposits, and hence, they are suited for substrates with complex 3D geometries. Additionally, the temperatures required are lower than those for PVD and hence smaller energetic costs are achieved. Tripathi [219–221] used $\text{Cu}(\text{thd})_2$ and $\text{Cr}(\text{acac})_3$ as metallic precursors and ozone as oxygen source in his ALD process. Films with optical transmission up to 80% were synthesized at temperatures as low as 250 °C with a growth rate of 0.2 nm s^{-1} . The films doped with 2.5% magnesium (using $\text{Mg}(\text{thd})_2$) presented high electric conductivities greater than 200 S cm^{-1} . Within the CVD process, the delafossite thin film grows from the surface reaction between precursors being decomposed (thermally or plasma assisted) within the volume of the reactor or at the surface when they undergo the surface reaction. Growth rates of 5 nm/min are obtained for medium-scale depositions (up to 20 cm) at temperature down to 400 °C [48]. The last method presented here is the spray pyrolysis (SP) [217, 222–224]. Similar to the CVD method, this is a simple technique that is suited to deposit films over large areas. The precursor solution is sprayed directed onto the heated substrate where after decomposition, the oxidation leads to a metal oxide deposition. Cu–Cr–O delafossite films were synthesized on various substrates at temperatures as low as 345 °C [223]. What must be emphasized here is that the last two methods (CVD and SP) lead towards Cu–Cr–O films presenting a delafossite crystalline structure but far from a 1:1:2 classical stoichiometry (*i.e.* important excess/deficit of Cu or/and Cr) [225, 226]. These films present very promising optoelectronic properties, and studies are focusing lately on understanding the physical processes within [213, 216].

To summarize, the Cu–Cr–O delafossite films are deposited using a large panel of methods. The standard CuCrO_2 films and the extrinsic doped (see extrinsic doping section) ones follow similar deposition procedures. The chemical sources of the components (Cu, Cr and the dopant) are initially mixed in

the right proportion, and then, the synthesis process is started. A good example is described in Okuda et al. [142] where $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ ($0 < x < 0.04$) of Cu_2O , Cr_2O_3 and MgO powders are initially weighed in order to ensure the right proportions ($\text{CuCrMg}_0\text{O}_2$, $\text{CuCr}_{0.95}\text{Mg}_{0.005}\text{O}_2$, $\text{CuCr}_{0.9}\text{Mg}_{0.1}\text{O}_2$, etc.). The situation is different in the case of the fabrication of defective delafossite (intrinsic doped) films. Non-equilibrium thermodynamic conditions must be achieved in order to stabilize the metastable states (with important deviances from the 1:1:2 stoichiometry). The fabrication methods able to provide this kind of thermodynamic environment are generally involving dynamic precursor injection (SP or DLI-MOCVD) or plasma (RF sputtering or plasma-enhanced CVD).

Optical properties

Typical values in the range of 30–70% are commonly reported for the optical through the delafossite Cu-Cr-O thin films within the visible wavelength range. However, this is not a reliable parameter for comparing optical properties of different films due to its thickness dependence (Lambert law $I(d) = I_0 \exp(-\alpha d)$). Additionally, the morphology of the films depends on the deposition methods and on the performed post-treatments. This influences the absorption processes, altering optical transition between bands, sub-bands or defects. Hereby, the optical band gap is mostly used for characterizing and comparing the optical response of the thin films as this is an intrinsic property of material, not depending on the geometry of the film. The first report (based on the photoelectrochemical measurements) of the CuCrO_2 band gap [176] indicates an indirect band gap of 1.28 eV with one indirect.

and one direct allowed transition at 3.08 eV and 3.35 eV, respectively. The optical absorption appearing near 3 eV is due to the band-to-band transition $\text{Cu}^{3d} + \text{O}^{2p} \rightarrow \text{Cr}^{3d} + \text{O}^{2p}$ (Fig. 4). The absorption around 2 eV is associated with $\text{Cr}^{3d}(t_{2g}) \rightarrow \text{Cr}^{3d}(t_{eg})$ transition due to the octahedral environment of chromium atoms (crystal field splitting) [212]. Figure 5 depicts the experimental band gaps reported over the literature (Supplementary information section Table S.II). The significant span for the band

Figure 5 Survey of reported indirect and direct experimental band gap values for Cu-Cr-O delafossite films. On X-axis: the chemical symbol of the dopant; Cr def—Cr deficiency; ND—non-doped; Off stoic—off-stoichiometric delafossite. In the brackets are the references from the article. A more detailed survey is presented in supplementary information section Table S.II.

gap's values is again a result of the diversity of deposition methods and post-treatments. These band gaps might be tailored by tuning the deposition parameters [214] or the level of doping [181, 220]. For example, both direct and indirect band gaps are influenced by the content of Mg within the Mg/CuCrO_2 . They decrease for concentrations of Mg up to 8% but an increasing is then observed for greater dopant content [181]. This was attributed to the band gap renormalization and Burstein–Moss effect induced by the dopant. Finally, a decrease in transparency might be possible due to the Cr d–d transitions between the split energy levels of partially filled Cr^{3d} shell [116]. The excitation of electrons from the lower to the upper of these levels might occur by absorbing photons in the visible range.

Transport properties

The most common methods for studying the transport properties in the delafossite materials are the four-point resistivity and the Seebeck coefficient. These allow the direct determination of the conductivity (when thickness is known) and the carrier concentration (presuming the charge transport

mechanism as known); these furthermore grant the calculation of the mobility ($\sigma = ne\mu$). The temperature dependency of these parameters gives important information related to the transport mechanism. The use of Hall effect for investigating this material is challenging and generally questionable due to the usually very low mobilities of charge carriers. It requires very high magnetic fields or complex mathematic models that are not always reliable [227].

Pure (undoped) CuCrO_2 shows a high resistivity due to low acceptor defects concentration and high acceptor energy levels [48]. The reported values depend mainly on the synthesis method. Poienar et al. [228] reported a conductivity of 0.003 S cm^{-1} in a single crystal fabricated by the flux technique, Yu [229] reported a value of 0.2 S cm^{-1} for films prepared using RF sputtering, whilst Sadik [206] measured a conductivity of 0.0001 S cm^{-1} for film grown by pulsed laser deposition. There is a general agreement that CuCrO_2 in pure phase presents low conductivities and only the non-stoichiometric or doped delafossite phases show decent electrical conductivity, higher than 1 S cm^{-1} . The maximum reported values in this case are 278 S cm^{-1} for a Mg–N co-doped delafossite [47] and 100 S cm^{-1} for a non-stoichiometric one [161].

Source of doping

Extrinsic doping

Many groups reported a significant improvement of electrical conductivity with the introduction of divalent cations at the Cr site. This is a result of the increase in the holes concentration due to the charge difference in the substituting site. This boost in conductivity has been linked to $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ and to $\text{Cr}^{\text{III}}/\text{Cr}^{\text{IV}}$ hole mechanisms [82, 103, 142, 149, 230].

The main role of the dopants is to increase the carrier concentration, without altering the delafossite structure. [47] As a general rule of thumb for the doping process, the smaller size difference between the dopant and the substituted cation and M cations, the easier will be to dope. Typically reported CuCrO_2 dopants are Ba, Ca, Cd, Co, Fe [193], Mg, Mn [231, 232], N, [47], Ni [233], Sc [157], Sn and Zn [182]. Among all these, the magnesium has been reported as the dopant leading to the best performance in electrical properties of delafossite. When

doping with a trivalent cation X^{3+} (isovalent doping), the resulting compound shows a mix of properties related to CuCrO_2 and CuXO_2 [234]. Although the carrier concentration is not modified ($3+$ replaced by $3+$), changes of electrical properties are often reported [148, 157]. This might be a result of the difference between the radii of the dopant and of the substituted atom. The internal stress induced this way might alter the band structure and consequently the electronic charge mobility, as already demonstrated for polycrystalline films of Ge [235], Si [166] or graphene [167]. Table 3 summarizes the studies related to the extrinsic doping of Cu–Cr–O delafossite.

Intrinsic doping

Point native defects are widely considered as the source of holes in pure stoichiometric delafossites. However, the cations' vacancies and the excess oxygen (interstitial) anions have high formation energies and therefore are counterbalanced by the native hole killers, such as anion vacancies [67].

a) Cu vacancies ($\text{V}_{\text{Cu}} \rightarrow \text{Cu}^0 + \text{h}^+$) [82]; they act as hole donors and introduce shallow acceptor states [249].

b) Oxygen interstitials (O_i) [250]—Intercalation with oxygen to form $\text{CuCrO}_{2+\delta}$ phases improves the conductivity. The excess of oxygen intercalates within the crystal structure, trapping electrons and thus leaving behind two states in the VB:

$$\text{O}_2(\text{g}) = 2\text{O}_i'' + 4\text{h}^+.$$

This defect is more noticeable for larger B cations, because a bigger lattice would accommodate more excess of oxygen. The intercalation of oxygen creates tail states in the band gap, reducing the transmittance. It is difficult to observe oxygen intercalation for small B cations, probably due to the small size that shrinks the lattice enough to impede O penetration [128]. This phenomenon is strongly dependent on the oxygen conditions and annealing throughout the film's deposition.

The energy formation enthalpy of various defects in CuCrO_2 was also evaluated with LDA, PBE, PBE + U or HSE06 theoretical approaches [82, 251] (see the explanations above, within the paragraph related to the structure of delafossite), and the results are summarized in Table 4. All methods indicate the chromium substitution by magnesium (Mg_{Cr}) the

Table 3 List of the main extrinsic dopants of copper chromium delafossite and their reported effects

Dopant	Doped delafossite reported characteristics	Refs.
Al ³⁺	Destabilizes the antiferromagnetic order of Cr ³⁺ and induces weak ferromagnetism. The randomness introduced by the substitution leads to a decrease in conductivity	[141, 143]
Fe ³⁺	Slight improvement of electrical and optical properties. The iron induces hole-mediated Fe ³⁺ –Cr ³⁺ super-exchange coupling responsible for the room-temperature ferromagnetism [236]. Note that Fe doping does not produce holes directly but modifies the delafossite structure, leading to more interstitial oxygen atoms inserted into the lattice of the delafossite. Superconductivity for Fe-doped CuCrO ₂ up to 118 K has been also reported	[148, 193, 236]
Mg ²⁺	Mg-doped CuCrO ₂ shows improved conductivity compared with most of other <i>p</i> -type TCOs. Mg ²⁺ substitutes the site of a Cr ³⁺ site, converting the Cu ¹⁺ into Cu ²⁺ ; Mg ²⁺ substitution at the Cr site decreases the resistivity and Seebeck coefficient. Mg ²⁺ dopant might act as a donor rather than an acceptor if it occupies a Cu ⁺ site rather than a Cr ³⁺ site	[193, 237–239]
Mg ²⁺ + Ag ⁺	The dopants are not localized between the grains. Mg ²⁺ substitutes Cr ³⁺ . Ag ⁺ substitutes Cu ⁺ . Electrical conductivity increases by a factor of 560	[240]
Mg + Mn	The presence of Mg ²⁺ leads to a mixed valence state Mn ³⁺ and Mn ⁴⁺ that induces a hole-mediated double-exchange mechanism Mn ³⁺ –Cr ³⁺ and Mn ³⁺ –Mn ⁴⁺ . Very interesting diluted magnetic semiconductor	[241]
Mg + Ni	Enhances thermoelectric properties	[150]
Mg + S	The presence of sulphur leads to higher values of the mobility	[242]
Mn	The material exhibits a ferromagnetic transition. Slight improvement of conductivity for Mn content up to 10%	[231, 243]
Mg + N(in the presence of N)	Although it cannot be detected in the films, the best reported optoelectronic electronic properties correspond to processes where the N ₂ is present during the deposition. It acts as an acceptor, inserting more hole carriers into the delafossite lattice the following way: $N = N_O^- + h^+$	[47, 210]
Ni	An increased electrical conductivity with Ni ²⁺ doping in CuCr _{1-x} Ni _x O ₂ was observed for $0 \leq x \leq 0.6$	[204, 233]
Rh	Good matching in oxidation states and ionic radii. ($r \text{ Rh}^{3+} = 0.66 \text{ \AA}$; $r \text{ Cr}^{3+} = 0.63 \text{ \AA}$). Weak ferromagnetism induced at low temperature	[244]
Sc	The local lattice distortion induces breaking of the residual magnetic degeneracy	[157, 245]
Sc + Mg	The Sc and Mg incorporation in the delafossite structure generates microstrains showing an anisotropic behaviour. (Sc, Mg) substitution gives additional space for oxygen intercalation	[157]
Sn	Apparition of Cr ³⁺ /Sn ⁴⁺ mixed states that affects the thermoelectric properties. Lowers the conductivity	[246]
Zn	Delafossite phase is maintained up to 3% content of Zn. Electrical conductivity increases with the Zn content	[182, 247]
Ti	A dilution of spin is observed. Magnetic properties are reported	[248]

most thermodynamically favourable, followed by copper vacancies (V_{Cu}) and oxygen interstitial (O_i).

A special attention is given lately to the off-stoichiometric delafossite materials that are characterized by significant excess/deficit of copper and/or chromium [161, 223, 225, 252]. Although they demonstrate important deviation from the standard 1:1:2 stoichiometry, the structural analysis (XRD, Raman, XPS) indicates still a delafossite structure. Ling et al. [226] reported the fabrication of Cr deficient ($CuCr_{1-x}O_2$; $0 < x < 0.1$) films fabricated via the

solid-state reaction method. They observed an electrical behaviour similar to the Mg-doped $CuCrO_2$, reporting a minimal resistivity of 2 k Ω cm for $CuCr_{0.92}O_2$. It was concluded that the increase in carriers' concentration is a result of the excess holes doped into the Cu sites by the Cr deficiency. (One missing Cr atom might create three holes.) Next in order, researchers using the chemical vapour deposition started to report the synthesis of Cu–Cr–O delafossite layers with a significant Cu deficiency. Farrell et al. [223] reported first such a material with

Table 4 Calculation of formation energy of different defects and Mg doping using different theoretical approaches

Defect	Calculation method	Enthalpy change (eV)	Refs.
V _{cu}	PBE	0.16	[82]
V _{cu}	PBE + U	0.95	[82]
V _{cu}	HSE06	1.45	[82]
V _{cu}	LDA	− 2.5	[251]
O _i	PBE	1.27	[82]
O _i	PBE + U	1.38	[82]
O _i	HSE06	1.63	[82]
O _i	LDA	− 2.1	[251]
Mg _{Cr}	PBE	− 0.54	[82]
Mg _{Cr}	PBE + U	0.46	[82]
Mg _{Cr}	HSE06	0.62	[82]
Mg _{Cr}	LDA	− 2.13	[251]

20% copper deficit when using spray pyrolysis and acetylacetonate precursors for copper and chromium in methanol. An electrical conductivity of 12 S cm^{-1} and an optical transmission of 55% were determined for 90-nm thin films. Furthermore, the same group reported the obtention of a $\text{Cu}_{0.4}\text{CrO}_2$ film with interesting opto-electronic properties [225]. Raman, XPS and XRD analyses confirm the delafossite structure. However, they observed an increased number of Cr–O octahedra in these Cu deficient films when compared to crystalline CuCrO_2 . Finally, off-stoichiometric copper chromium delafossite showing simultaneously a copper deficiency and a chromium excess (i.e. $\text{Cu}_{1-x}\text{Cr}_{1+x}\text{O}_2$) was also synthesized using dynamic liquid injection—MOCVD [48, 215]. These films present a very peculiar 2/3:4/3:2 stoichiometry with one-third of the copper atoms missing and a supplementary one-third of chromium atoms. Up to now, these films show the highest values of conductivity (102 S cm^{-1} [161]) for a non-intentionally doped copper chromium delafossite.

Nevertheless, it is clear that the source of doping in these last off-stoichiometric delafossite materials cannot be related to (only) point defects and actual research trying to understand the charge source and transport mechanism within such particular materials is still conducted. Only recently, chains of Cu vacancies were observed [161] for the first time and investigated as an eventual source of doping in such materials. By using positron annihilation spectroscopy on $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$ samples, Lunca-Popa et al. [213] associated the decrease in conductivity with a

decrease in size of the chained vacancies. They suggest therefore the presence of a ripening mechanism based on the dissolution of the chains of copper vacancies being healed upon annealing, leading to a drop of electrical conductivity. The presence of these metallic chained vacancies is supported by the theoretical work of Art and Zunger [253, 254] showing that in the case of transparent conductors, the law of definite proportion can be broken and the formation of these type of defects is favoured thermodynamically as “it costs no energy”.

Howbeit, despite the significant differences between extrinsic doped CuCrO_2 and highly conductive $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$, there are important similarities on their electric properties. For example, in the case of Mg/CuCrO_2 , Okuda [142] finds different Seebeck effect temperatures dependencies ($S = f(T)$) (Fig. 6a) for non-doped ($x = 0$) and doped delafossite. The S value for $x = 0$ is about $350 \mu\text{V K}^{-1}$ at 300 K, whilst the T dependence shows a broad peak structure. The Seebeck coefficient decreases drastically with the increase of Mg content. The broad peak structure in the T dependence gradually disappears with x . Starting with a Mg content of 2%, the Seebeck coefficient is nearly proportional (linear dependence) with the temperature up to 300 K that corresponds to a decrease in the resistivity. A similar behaviour was observed within $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$ delafossite films (Fig. 6b). As-deposited samples present an almost a linear dependence on T . After annealing, the curve

Figure 6 Temperature dependence of the Seebeck coefficient for: $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ (black) ($x = 0$ and 0.05) and $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$ (red) (as-deposited and annealed). Data from [142] and [161].

Nevertheless, the delafossite has been consistently proposed to exhibit electrical transport limited by small polaron hopping [83, 103, 126, 196, 215, 256, 257]. This can be justified by the high effective mass, due to the polaronic interaction between carriers and the lattice. In the case of small polaronic conduction, the distortion of the lattice extends over distances smaller than the lattice constant. The strong interaction between the lattice and the carrier leads to a charge self-trapping due to their own polarization. Polaron conduction is characterized by hopping properties. In contrast to other conduction mechanisms, lattice vibrations do not inhibit conduction but rather allow it, like as in ionic conductivity. There are two types of polarons; in the case of large polarons, the distortion of the lattice extends over few lattice constants. The carrier transport is still called “band conduction” like classical semiconductors, but the effective mass at the VBM or CBM is much higher due to the polaronic interaction between carriers and the lattice [258, 259]. For small polarons, the distortion of the lattice extends over distances smaller than the lattice constant. The coupling is strong enough, and the carriers become self-trapped by its own polarization generated in the ionic lattice [260]. It should be emphasized here that the $T^{-1/4}$ temperature dependence is not automatically implying the solely presence of small polaron mechanism. According to calculations, other conduction mechanisms, using specific presumptions, can also show a temperature dependence similar to the $T^{-1/4}$ dependence [261–263]

Anisotropy of electronic properties

It has been reported that the crystalline structure of delafossites has a large anisotropic electrical conductivity, with the in-plane (ab) conductivity (σ_{ab}) being far larger than along the c-axis (σ_c) [249]. CuCrO_2 was reported with a resistivity ratio of $\rho_{c \text{ axis}}/\rho_{ab \text{ plane}} \approx 35$ at 300 K, implying that $[\text{CrO}_2]$ and/or $[\text{Cu}^+]$ planes are better conducting path than Cu–O–Cu along c-axis [228]. According to electronic structure calculations performed (Fig. 4) for CuCrO_2 , the d orbitals of Cr^{3+} are mainly contributed near the Fermi level as compared to those of Cu^+ , which could imply that the carriers would be mainly in the Cr planes rather than in the Cu ones. An increase in the

(00l) orientation implies a greater presence of Cu + (ab planes) in the conduction path [210].

Thermoelectric measurements

The debate concerning the mechanism governing the conduction in heavily doped delafossites is still active. According to the of Bosman-Van Daal [264] limit, small polaron transport is considered to occur for low mobilities, below $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Such low values are burdensome to be determined by the Hall effect as very high magnetic fields or complicated mathematical model are required. For example, O’Sullivan et al. [265] measured a mobility of $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 10% Mg/ CuCrO_2 at 300 K by using a magnetic field of 14 T. Moreover, Werner et al. [227] engaged a complex model for off-set Hall coefficient corrections and estimated a mobility of $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for off-stoichiometric $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$ [215].

In order to circumvent the use of the Hall effect, thermoelectric measurements can be used. This allows to extract the carrier concentration and, when combined with resistivity measurements, the estimation of mobility values ($\sigma = ne\mu$). However, this method raises some debate regarding the approximation done for the effective density of states. For instance, in the case of ZnRhO_2 , a polaron conduction is demonstrated if the effective density of states is assumed constant, whilst band conduction properties are observed if a temperature dependence is assumed [266]. The Seebeck coefficient is defined as $\Delta V / \Delta T$, where ΔV is the induced thermoelectric voltage as in response to a temperature difference ΔT across the material. If the energetic structure of a material is known, the position of the Fermi level can be thus deduced from the Seebeck coefficient. Furthermore, the charge carrier concentration can be determined assuming a known charge transport model. For the p-type semiconductors, the most often reported conduction models are the non-degenerate [267] and degenerate [268, 269] semiconductor or small polaron [258, 270, 271]. The relationship between the Seebeck coefficient and the carrier concentration in each of these cases has the following expression:

$$\text{Non-degenerate model } S = \frac{k_B}{e} \left(\ln \left(\frac{N_V}{p} \right) + A \right) \quad (4)$$

$$\text{Degenerate model } S = \frac{82\pi^2 T k_B^2 m^{2*}}{3eh^2} \left(\frac{\pi}{3p} \right)^{\frac{2}{3}} \quad (5)$$

$$\text{Small polaron model } S = \frac{k_B}{e} \ln \left[\frac{2(1-c)}{c} \right] \quad (6)$$

where h is the Planck constant, k_B is the Boltzmann constant, N_V is the effective density of states, A is a constant depending on the nature of scattering process ($1 < A < 4$; $A = 0$ for small polaron model), e is the electron charge, p is the carrier concentration, m^* is the effective mass, T is the absolute temperature and c is the fraction of occupied sites by polarons.

As emphasized before, the small polaron mechanism onto Cu planes is the most often used to explain the charge transport within the delafossite. Within the formula above, for the Cu–Cr–O delafossite the fraction of occupied sites can be written as $c = [\text{Cu}^{2+}] / [\text{Cu}^+]$, where $[\text{Cu}^{2+}]$ is the number of occupied sites by polarons and $[\text{Cu}^+]$ is the concentration of copper atoms in a delafossite crystal.

Figure 8 depicts a summary of Seebeck coefficient and electric conductivity reported values in the literature. It can be seen that the highest conductive samples demonstrate the lowest Seebeck coefficients (typically below $200 \mu\text{V K}^{-1}$). This is the case of doped or off-stoichiometric Cu–Cr–O delafossites. For pure delafossite or generally, for low conductive delafossite films, values of thermopower coefficient are beyond $500 \mu\text{V K}^{-1}$. These reports might induce

Figure 8 Compilation of Seebeck coefficient and corresponding electric conductivity reported values for Cu–Cr–O delafossite. In the brackets are the references from the article. A more detailed survey is presented in Table S.II (supplementary information).

the idea that the high conductivity is driven by the big number of charge carriers (inversely proportional to S), whilst a direct influence of mobility is difficult to be extracted. Seebeck coefficient depends also on the temperature range. The Seebeck temperature dependence shows specific trends for the undoped and doped Cu–Cr–O delafossite (Fig. 7). In the case of low conductive delafossite thin films, the Seebeck coefficient decreases with the temperature, whilst an opposite trend is observed for highly conductive doped samples. Some deviations are observed below the room temperature due to the transition between the conduction mechanisms.

Carrier concentration and mobility

A plot of mobility versus carrier concentrations of undoped and doped copper chromium delafossite thin films reported in the literature is illustrated in Fig. 9. The conductive films are usually characterized by high levels of carrier concentration ($> 10^{20} \text{ cm}^{-3}$), typically featuring a degenerate semiconductor. The maximal reported values of holes concentration are around 10^{21} – 10^{22} cm^{-3} [142, 161, 265] for doped films fabricated by various methods. On the opposite, low carrier concentrations are describing the samples with low conductivity. Values below 10^{17} cm^{-3} are reported for low conductive, non-doped delafossite

Figure 9 Compilation of carrier mobilities and the corresponding concentration reported values for Cu–Cr–O delafossite. In the brackets are the references from the article. A more detailed survey is presented in supplementary information section—Table S.II.

Table 5 Calculated values of carrier concentration and mobility using different models

Measured conductivity	$\sigma = 0.7 \text{ mS cm}^{-1}$		$\sigma = 102 \text{ S cm}^{-1}$	
	Small polaron	Non-degenerated	Small polaron	Degenerated
$p \text{ (cm}^{-3}\text{)}$	$1.4 \cdot 10^{17}$	$1.3 \cdot 10^{17}$	$1.5 \cdot 10^{21}$	$3.4 \cdot 10^{21}$
$\mu \text{ (cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$	0.067	0.072	0.33	0.15

with a minimal value of 10^{14} cm^{-3} for CuCrO_2 [84]. Most of the mobilities values are calculated from thermoelectric measurements (as described above, a direct measure using Hall effect is difficult) by using the $\sigma = ne\mu$, with the concentration estimated from the Seebeck coefficient. Its expression depends on the transport model considered, and one might think that assuming a wrong model will lead to erroneous values for electronic parameters. This is not entirely true as shown in the next example. In [161], the authors investigate (at room temperature) two Cu–Cr–O samples with different conductivities (102 S cm^{-1} and 0.7 mS cm^{-1} , respectively). After a direct measure of sheet resistance and Seebeck coefficient, different transport models are used to estimate the carrier concentration and finally the mobility. The results are presented in Table 5. In the case of conductive sample, the use of small polaron model or degenerated semiconductor leads to comparable (same order of magnitude) values for p and μ . The same similarity is observed when the small polaron or non-degenerate semiconductor model is applied for low conductive samples. This invariance with the choice of the model enhances the reliability of data obtained from thermoelectric measures.

Conclusion

The CuCrO_2 shows the highest p-type electrical conductivity among delafossite oxides. This contravenes [219] the tendency observed for several other CuMO_2 ($M = \text{B, Al, Sc, Y}$) delafossites where a decrease in electrical conductivity with increasing size of the M^{3+} cation is observed. This discrepancy might be a result of the favourable covalent mixing between Cr^{3+} and O^{2-} and of the high density of Cr^{3d} states near the VBM. The values of electronic properties depend on the morphology of the film, which is strongly correlated with the deposition method. The

pure delafossite phase demonstrates very low electrical conductivity. On the contrary, the off-stoichiometric phases and those doped with magnesium show electrical conductivities of hundreds of S cm^{-1} . These values are a result of the high level of concentration carriers induced by the defects. The most used model used for explaining the charge carrier transport mechanisms is the small polaron, which might explain the low values of the electronic mobility. However, the degenerate or non-degenerate semiconductor models convey for reliable results in the case of high or, respectively, low conductive delafossite phases. There are two main prospective strategies for ameliorating the actual electrical performances of delafossite material. A first one resides in improving the very small carriers mobilities by manipulating the energy band structure of the material. This can be done, for example, by engineering the strain of the films as was already proven in for other semiconductors. A second strategy might be based on the doping of the off-stoichiometric Cu–Cr–O delafossite materials. This approach was fruitful on the case of standard 1:1:2 stoichiometry whereby the doping with 5% Mg led to two orders of magnitude increase in the electrical conductivity. A similar result might be expected than for an adequate doping of a defective delafossite material. This review provides convincing arguments that Cu–Cr–O delafossite materials are among the most suitable chemistry for the development and integration of functional transparent p-type semiconductors. The unique capability in adjusting the stoichiometry, the defects features, the residual stress of thin films together with the capability to grow well-controlled layers is still opening many routes of research to harness the full potential of such a complex material in real device applications.

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Author contributions

PLP and MM conceptualized the article. PLP and DL participated to funding acquisition and project administration. PLP, MM and JA wrote the first draft. MM, JC and JA performed the data curation. All authors participated to the review and the editing of the final manuscript.

Declarations

Conflict of interest The authors declare no conflict of interest.

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