

| | a | c | Ref. |
|--|--------|---------|----------------|
| α -Al ₂ O ₃ | | | |
| α -Cr ₂ O ₃ | 4.96 Å | 13.59 Å | Mi et al. 2018 |
| α -Ga ₂ O ₃ | | | |

Table 1: Lattice constants of selected corundum structured compounds.

Chromia (Cr₂O₃) is a sesquioxide composed of the transition metal chromium and oxygen. Among other chromium oxides (e.g. metallic CrO₂, toxic CrO₃ etc.), it is the thermodynamically most stable phase [1–3], making it the abundant chromium oxide on earth [4]. Cr₂O₃ occurs mainly in the α -phase (described below), but a cubic spinel γ -phase with random missing Cr point defects has also been reported [2]. Henceforth, “Cr₂O₃” will refer to the α -phase.

As coating material, Cr₂O₃ is commonly used due to its high hardness and resistance against corrosion [3, 5], also explaining its use-case as component of stainless steel to form passive films [1]. Cr₂O₃ absorbs electromagnetic waves with wavelengths smaller than 400 nm, making it opaque in the UV-spectrum [6, 7]. It is transparent in the visible spectrum with a transmittance of 50 % at 800 nm [6].

Cr₂O₃ crystallizes in the corundum structure, which has trigonal symmetry (space group $R\bar{3}c$) and belongs to the hexagonal crystal family. One unit cell contains six formula units, i.e. 12 chromium cations and 18 oxygen anions [1]. The oxygen atoms arrange in a hexagonal close-packed manner, where two thirds of the formed octahedrons are filled with Cr atoms [8]. The unit cell is spanned by a principal axis, called c -axis¹, and a hexagonal basal plane with lattice constant a . The numerical values for those lattice parameters differ depending on the publication [4, 9, 10], and we will use the values in Tab. 1.

Several techniques were applied for depositing chromia thin films, including: Chemical Vapor Deposition (CVD) [11–13] on silicon and glass, thermal evaporation on platinum [2], electron-beam evaporation on glass [3], radio-frequency (RF) sputtering on sapphire [9, 14, 15], reactive direct current (DC) sputtering on glass [7], and reactive [16] and non-reactive [5] Pulsed Laser Deposition (PLD) on silicon and glass, respectively.

Electronic Structure Experimental and theoretical studies reveal that chromia exhibits a band gap of 3.2 to 3.4 eV [1, 2, 4]. This predicts insulating behavior, classified as both Mott-Hubbard type and charge-transfer type, which are models to describe the electronic behavior of compounds containing transition metals with partly filled $3d^n$ orbitals² [1, 4, 8]: Density Functional Theory (DFT) calculations show that the Cr- $3d$ states are almost solely responsible for electronic states in the conduction band and that they are also present in the valence band [1, 4]. Thus, $3d \rightarrow 3d$ band transitions are possible, favoring the Mott-Hubbard model of this compound [1]. Furthermore, the O- $2p$ states are mainly present in the valence band, at similar energies as the Cr- $3d$ states, which leads to hybridization and thus favoring the charge-transfer model [1].

However, several studies agree on Cr₂O₃ being a semiconductor with p -type conduc-

¹The spins of the Cr atoms along this direction are alternating \uparrow and \downarrow , making the crystal antiferromagnetic.

² $n = 5$ for Cr

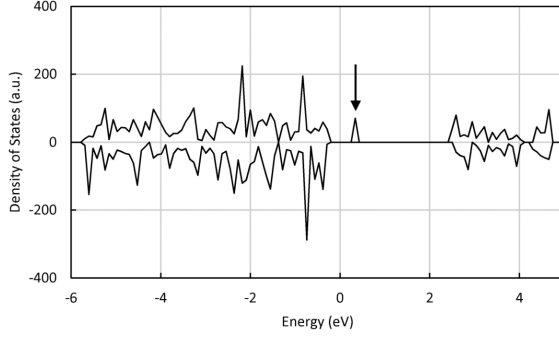


Figure 1: Calculated density of states (DOS) of chromia, taking a V_{Cr} into account. The arrow marks the new acceptor level. Image taken from [1].

tivity³ at room temperature and atmospheric conditions [1, 4–6, 14, 16, 17]. Calculating the impact of different crystal point defects on the band structure may give insight into these observations. Indeed, when considering a missing chromium atom (“vacancy” V_{Cr}) the band structure changes in two ways: The band gap itself is reduced [4], but not in a way that it would make excitations of valence electrons into the conduction band much more probable than at room temperature. But additionally, there is a new band introduced slightly above the Fermi level (cf. Fig. 1), which acts as an unoccupied acceptor level [4]. This defect state is mainly composed of O-2*p* orbitals of the oxygen anions surrounding the vacancy [1]. From a more intuitive point of view, a missing neutral chromium atom effectively removes the Cr^{3+} cation as well as three electrons bound to the adjacent O^{2-} anions, thus creating three holes [1] explaining the *p*-type conductivity.

Note that there are also other possible defects with different effects: a chromium Frenkel point defect describes a Cr atom leaving it’s position and occupying a formerly unoccupied oxygen-octahedron. This Frenkel defect actually creates a new band right below the Fermi level, acting as an occupied donor level [1]. A similar defect state is introduced by oxygen vacancies [4]. But note that the Fermi level is located only slightly above the Valence Band Maximum (VBM) and thus the new occupied donor level is not significantly closer to the Conduction Band Minimum (CBM), which means that electrons still have to overcome the band gap energy to get into conducting states. This favors the formation of holes via Cr vacancies (O-2*p* acceptor states) rather than electrons via Cr Frenkel defects and O vacancies (Cr-3*d* donor states).

³Cheng et al. (2001) actually find Cr_2O_3 to be insulating. It is noted that they examined Cr_2O_3 as an 2 nm thick oxide surface on CrO_2 films deposited by CVD.

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