

Identification and Quantification of Boron Dopant Sites in Antiferromagnetic Cr₂O₃ Films by Electron Energy Loss Spectroscopy

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Cr₂O₃ is antiferromagnetic in bulk but ferromagnetic on the (0001) surface. Bulk Cr₂O₃ has two degenerate antiferromagnetic states that can be switched by an electric field, which also switches the (0001) surface magnetism [1], creating the potential for voltage-controlled magnetic data storage and spintronic data processing. However, the magnetic ordering (Néel) temperature of pure Cr₂O₃ is too low for microelectronic applications. Boron substituting for oxygen in Cr₂O₃ to form BCr₄ tetrahedra increases the exchange energy of neighboring Cr atoms from the favorable hybridization geometry [2], increasing the Néel temperature.

We have combined electron energy loss spectroscopy (EELS) fine structure and density functional theory (DFT) calculations to determine the structure of B dopants in Cr₂O₃ thin films. EELS is highly sensitive to the nature of chemical bonds and to an atom's coordination environment. Especially for doped oxides when the dopant is surrounded by strong backscattering O atoms, EELS is dominated by scattering events within the local neighbours that can be explained by a molecular approach [3]. We find B in BCr₄ tetrahedra, but also in distorted BO₃ triangles. The BO₃ triangles can be identified by manipulating the electron momentum transfer (q) in EELS, which changes the differential cross sections for the 1s- π^* and 1s- σ^* transitions. BCr₄ tetrahedra can be identified and also quantified by linear combination of simulated B K edges to reproduce the experimental π / σ ratios.

Figure 1(a) is a HAADF STEM image of a 2.5% B doped Cr₂O₃ film on Al₂O₃ substrate. Both the B and O atoms are invisible due to relatively weak high-angle scattering cross section. Figure 1(b) is a map of the B K edge intensity, showing a uniform distribution of B in the Cr₂O₃ film. Figure 1(c) is the B K edges acquired from plan view (top) and cross section (bottom) zone axes. The 194 eV peak corresponds to the 1s- π^* transition and the 203 eV peak corresponds to the 1s- σ^* transition [4]. The typical geometry of the B sp² hybridization forms BO₃ triangles with σ bonds parallel to the BO plane and π bonds normal to the BO plane [3]. The B K edges show clear orientation dependence because of the significant directionality of unoccupied 2p states of the BO₃ sp² structure. As illustrated in Figure 1(d), with the large EELS collection angles used in this experiment, the π intensity is proportional to the projection of the momentum transfer q onto the corresponding orbital orientations [4]. This indicates the BO₃ plane is normal to the [0001] direction.

Figure 2(a) is the possible B dopant structures, relaxed by DFT. All the structures shown have relatively low formation energies (± 2 eV) calculated by Zhang-Northrup formalism [5] under film growth conditions, so they are thermodynamically accessible. The simulated BO₃ structures are either planar or slightly distorted, but all of them are normal to the [0001] directions, which matches with the EELS results in Figure 1(d). The existence of BCr₄ can be confirmed by the distinct π / σ ratios from multiple-scattering EELS simulation in Figure 2(b), especially on the plan view zone. The bounds of the

functional BCr_4 out of the total B can be probed by linear combination of simulated BCr_4 K edges with each BO_3 K edge to reproduce experimental π / σ ratios, which is shown in Figure 2(c). Only 12%-43% B dopants form BCr_4 tetrahedra and increases Néel temperature. Further calculation shows that the other BO_3 structures can frustrate the bulk antiferromagnetic order and suppress the interface exchange bias. To make B doping more efficient, posting annealing under low oxygen partial pressure will favor the formation of BCr_4 , and co-doping is also a promising approach to stabilize BCr_4 [5].

References:

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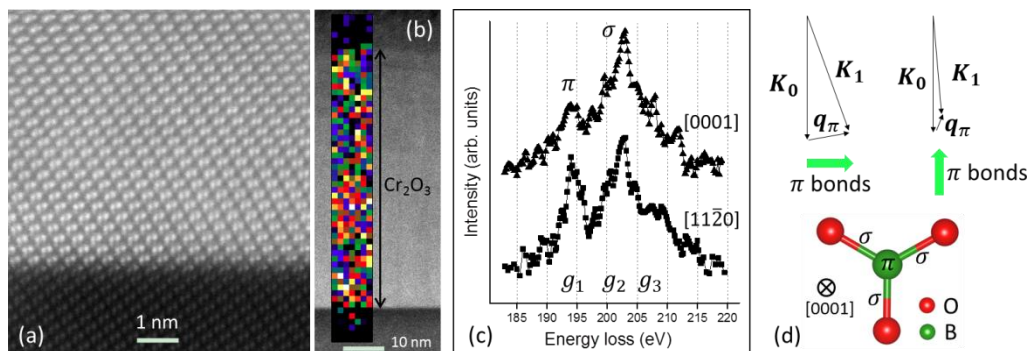


Figure 1. (a) HAADF STEM image of a B doped Cr_2O_3 film on Al_2O_3 substrate. (b) EEL spectrum guide image showing the whole 80 nm thick Cr_2O_3 film with B K edge intensity map superimposed. (c) B K edges from plan view and cross section zone axis. (d) Schematic illustration of EELS momentum transfer and the suggested orientation of BO_3 triangles.

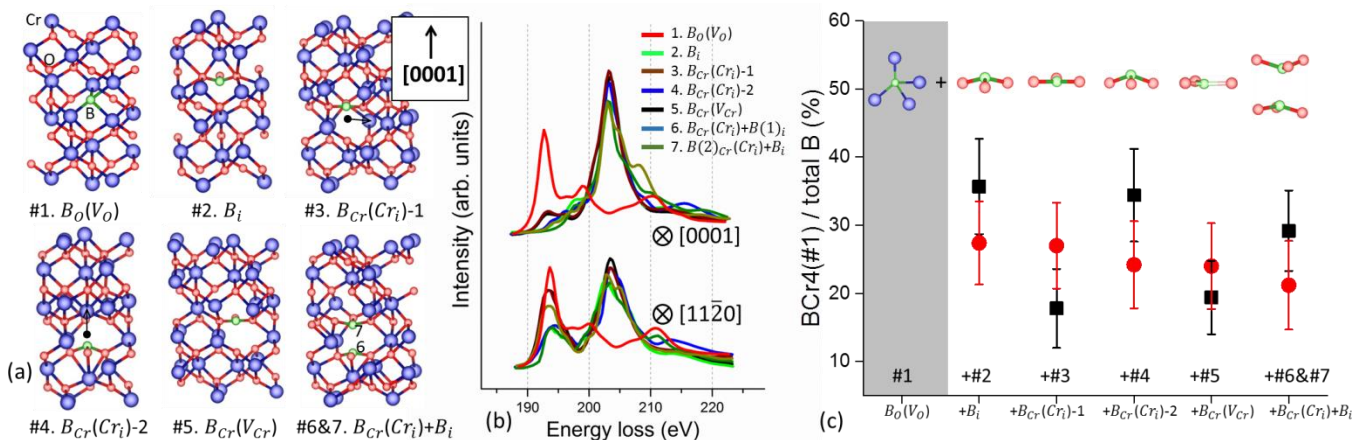


Figure 2. (a, and b) Calculated B dopant structures and corresponding EELS from multiple scattering simulations. (c) Quantification of the functional BCr_4 tetrahedra (#1. $\text{B}_\text{O}(\text{V}_\text{O})$) / total B by linear combination of simulated BCr_4 K edges with each BO_3 triangles K edges to reproduce the experiment π / σ ratio. Black symbols are from the cross section data, and red symbols are from plan view data.