

## Synthesis, characterization and modeling of $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ (111) epitaxial thin films

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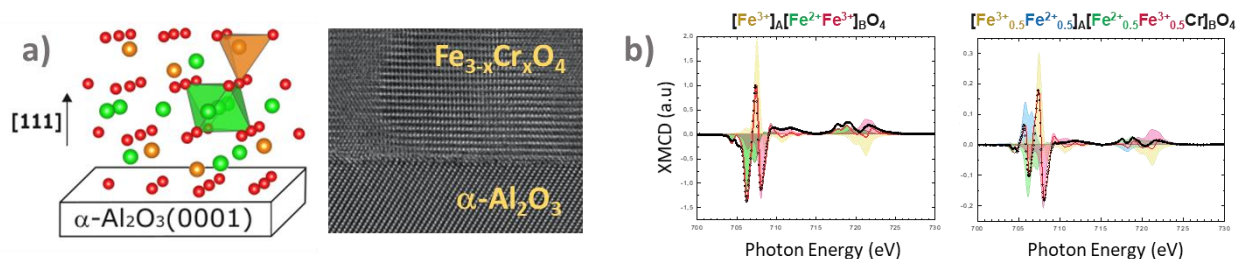
In the search for novel materials, oxides with spinel structure ( $\text{AB}_2\text{O}_4$ ) are very attractive due to their unique physicochemical and magnetic properties. The flexibility of the spinel structure offers the possibility to tailor their functional properties by incorporating different cations into the host lattice. In this regard, the  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  spinels are of considerable interest. This series forms a complete solid solution intrinsically defect free for the  $0 \leq x \leq 2$  range, in which the two limiting compositions have highly distinct physicochemical and magnetic properties. Whereas  $\text{Fe}_3\text{O}_4$  is a typical ferrimagnetic half-metal material,  $\text{FeCr}_2\text{O}_4$  is an insulator with low Curie temperature and conical spin structure. As potential materials of high magnetoelectric effect and adjustable band gap, the  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  solid solution has attracted attention for applications in many fields, like spintronic [1] and photocatalysis [2].

Although the growth of thin films is key for modern applications in electronic and spintronic devices, previous works on the electronic, magnetic and photoconductive properties of the  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  solid solution are based on bulk-like samples. Herein, we have performed a comprehensive study of the effect of substitutional Cr on the physical properties of high quality  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  epitaxial thin films. The aim is to understand the effects of increasing Cr content on the physicochemical properties of these thin films, which may strongly deviate from the bulk depending on film thickness, surface and/or interface effects.

To do so, epitaxial  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  layers (Figure 1a) have been grown in a dedicated atomic Oxygen assisted Molecular Beam Epitaxy (O-MBE) setup [3]. Each sample has been thoroughly characterized by core level spectroscopies (XPS, XAS, XMCD), X-ray diffraction, transport, magnetometry and electron microscopy. In order to improve interpretation of experimental data, we have performed molecular modeling and atomistic simulations. This dual experimental and theoretical approach opens the way to understanding at atomic level the changes in the physicochemical properties of  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  thin films while  $x$  increases.

Evolution of functional properties depends mainly on the Fe and Cr local structure, *i.e.* valence, distribution among the cation sublattices, and relative strength of competing effects. By means of XMCD analysis and Crystal Field Multiplet simulations (Figure 1b), we show that  $\text{Cr}^{3+}$  ions replace  $\text{Fe}^{3+}$  ions at octahedral sites (B) of magnetite, whereas  $\text{Fe}^{2+}$  ions are displaced from octahedral to tetrahedral sites. Primary effects are then: (i) the decrease of the average magnetic moment at the B sites, and (ii) the blocking of the B-site electron hopping path typical of  $\text{Fe}_3\text{O}_4$ , favoring a new conduction mechanism. The observed tendencies are promising and congruent with the literature [4].

- [1] I. Žutić et al., Rev. of Mod. Phys. 76, 323 (2004); [2] F. Magalhães et al., Appl. Cat. A: General. 332, 115 (2007); [3] J.-B. Moussy, J. of Phys. D: Appl. Physics. 46, 143001 (2013); [4] Ma J et al., Phys. Rev. B. 89, (2014).



**Figure 1:** (a) Schematic representation of  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  epitaxial thin films grown on sapphire (left) and their corresponding HRTEM image (right). (b) XMCD experimental and calculated spectra at the Fe  $L_{2,3}$  absorption edge for  $\text{Fe}_3\text{O}_4$  (left) in comparison of  $\text{Fe}_2\text{CrO}_4$  (right) layer measured at 300K in a magnetic field of 2 T.