

# Atomic scale charge compensation mechanism in Ca and Y co-doped bismuth iron garnet thin films

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Bismuth iron garnet (BIG)  $Bi_2^{3+}Fe_5^{3+}O_{12}^{2-}$  is an insulating [1,2] ferrimagnet oxide with outstanding magneto optical properties [3] that can only be obtained as nanostructures. We synthesised crystalline thin films of calcium and yttrium co-doped bismuth iron garnet (CaY:BIG,  $Bi_{2.5}^{3+}Ca_x^{2+}Y_{0.5-x}^{3+}Fe_5 O_{12-\delta}$ ) with the aim of creating new magnetic semiconductors. The  $Ca^{2+}$  is expected to substitute the  $Bi^{3+}$  site in order to induce  $Fe^{3+/4+}$  mixed valence states toward hole doping. The Bi content is kept constant to control the magneto optical properties. Improved electrical conductivity, more than 7 orders of magnitude higher than yttrium iron garnet was obtained. The relationship between these physical properties and the impact of local doping level is still unclear.

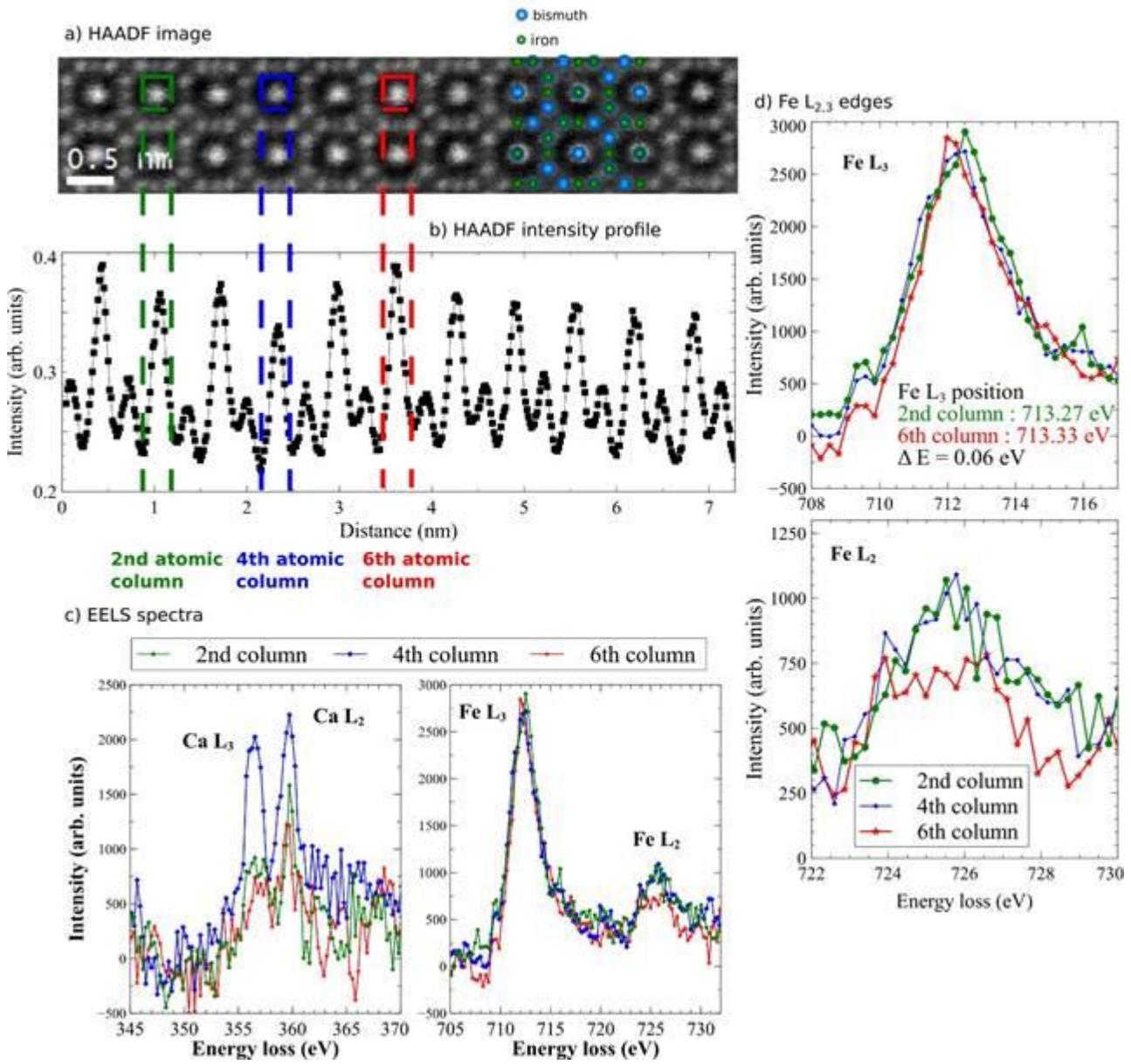


Fig 1. a) STEM-HAADF image of  $Bi_{2.5}Ca_{0.3}Y_{0.2}Fe_5O_{12-\delta}$ . b) Intensity profile of a). c) Extracted spectra at Ca-L2,3, O-K and Fe-L2,3 edges on a few atomic columns indicating the Ca presence, i.e. 4<sup>th</sup> column, or not. d) Zoom on the Fe-L2,3 showing energy shift of Fe-L3 barycenter in L3 edge and intensity difference in L2 edge.

Since it exists no bulk form of these BIG-based phases, transmission electron spectro-microscopy (STEM/EELS) is a key technique for such problematic. The main challenge is to assess the electrical conductivity's origin in relation with minor local stoichiometric evolution of Y, Ca and O. Another difficulty resides in the quantitative measurement of  $Fe^{3+}/Fe^{4+}$  ( $Fe^{4+}$  is of ligand hole character) due to  $Ca^{2+}$  substitution and the occurrence of  $Fe^{2+}/Fe^{3+}$  (both are of ionic character) induced by oxygen vacancy creation. The experiments were performed on a Cs corrected Nion UltraSTEM 200 operated at 100kV with 30 mrad convergence angle, 50 mrad EELS collection angle and around 50 pA of probe current. EELS data were acquired using an EELS Gatan spectrometer modified with an electron multiplying CCD as a final detector. Such system allow a fast, i.e. up to 8MHz read-out frequency, and efficient, i.e. up to electron counting, detection.

Average Ca/Fe ratio of 5% and Y/Bi ratio of 14%, close to the expected values, were confirmed in the film by probing Ca-L (350 eV), Fe-L(710 eV), Y-L (2080 eV), Bi-M (2580eV) EELS edges and no evidence of Ca clusters were observed. Down to the atomic scale, darker columns in HAADF contrast (Fig. 1 b) are observed and exhibit higher Ca content. The Ca substitutes well within the garnet matrix. On a few probed atomic columns, a clear shift of the Fe L3 absorption edge and an increase of L3/L2 intensity ratio (Fig.1 d) on identical crystallographic sites indicating a local change of electronic density of states [4, 5] were observed. This effect does not appear to correlate with Ca content. Electron doping seems to be the prevailing effect in this film, certainly due to the presence of oxygen vacancies, which are counterbalancing the Ca doping effect. Advanced and precise STEM-EELS studies enable us to understand better the charge compensation mechanism and the quantification of charge transfer to correlate further with their macroscopic physical properties.

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