Atmosphere-Induced Reversible Resistivity Changes in Ca/Y-Doped Bismuth Iron Garnet Thin Films

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Bismuth iron garnet $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ (BIG) is a multifunctional insulating oxide exhibiting remarkably the largest known Faraday rotation and linear magnetoelectric coupling. Enhancing the electrical conductivity in BIG while preserving its magnetic properties would further widen its range of potential applications in oxitronic devices. Here, a site-selective codoping strategy in which Ca$^{2+}$ and Y$^{3+}$ substitute for Bi$^{3+}$ is applied. The resulting p- and n-type doped BIG films combine state-of-the-art magneto-optical properties and semiconducting behaviors above room temperature with rather low resistivity: 40 $\Omega$ cm at 450 K is achieved in an n-type Y-doped BIG; this is ten orders of magnitude lower than that of $\text{Y}_3\text{Fe}_5\text{O}_{12}$. High-resolution electron spectromicroscopy unveils the complete dopant solubility and the charge compensation mechanisms at the local scale in p- and n-type systems. Oxygen vacancies as intrinsic donors play a key role in the conduction mechanisms of these doped BIG films. On the other hand, a self-compensation of Ca$^{2+}$ with oxygen vacancies tends to limit the conduction in p-type Ca/Y-doped BIG. These results highlight the possibility of integrating n-type and p-type doped BIG films in spintronic structures as well as their potential use in gas sensing applications.

1. Introduction

In transition metal oxides (TMO), the strong interplay between their lattice, charge, spin, and orbital degrees of freedom can be fine-tuned to produce outstanding physical properties that yield a plethora of functionalities$^{[1,2]}$ such as ferroelectricity, multiferroicity, superconductivity, thermoelectricity, and resistive switching. However, few complex TMOs such as the prototypical system $\text{Fe}_3\text{O}_4$ possess simultaneously strong magnetism and significant electrical conductivity.$^{[4]}$ In this work, we aim at combining in a single oxide phase relatively high electrical conductivity and robust magnetism at room temperature while preserving its initial functionalities. Bismuth iron garnet (BIG), i.e., $\text{Bi}_3\text{Fe}_5\text{O}_{12}$, is a promising candidate material, which presents multiple remarkable physical properties for achieving these goals. BIG crystallizes in the Ia-3d cubic space group and presents uncompensated magnetic moments on Fe$^{3+}$ ions occupying 16 octahedral (Oh, spin down) and 24 tetrahedral (Td, spin up) sites, resulting in strong ferrimagnetism, while 24 Bi$^{3+}$ ions are located in the dodecahedral sublattice. The resulting significant net magnetization of BIG (1600 G at 300 K)$^{[5]}$ is preserved up to 660 K.$^{[6]}$ Furthermore, BIG possesses the largest known Faraday rotation, i.e., $-17^\circ\mu\text{m}^{-1}$ at 580 nm.$^{[7]}$ Efficient magneto-optical (MO) photonic crystals$^{[8,9]}$ and optical isolators$^{[10]}$ based on BIG systems have already been developed successfully. More recently, a linear magnetoelectric coupling was reported in this system at room temperature and above.$^{[11]}$ However, like all iron garnet phases, stoichiometric BIG is an insulator. Interestingly, density functional theory calculations$^{[12,13]}$ predict BIG to be an insulator with several spin gaps in both the valence and the conduction bands, as confirmed via optical absorption experiments.$^{[14]}$ All these features make BIG a potential candidate as a multifunctional material for oxide-based electronics and tailoring its transport properties from insulator to semiconductor will provide new perspectives of integration into magnetoplasmonic structures or spin-polarized BIG-based heterostructures. The present work focuses on enhancing the electrical properties of substituted-BIG phases by applying a site-selective cosubstitution strategy with Ca$^{2+}$ and Y$^{3+}$ in dodecahedral Bi sites. Ca substitution aims at improving BIG’s electrical conductivity via the introduction of hole charge carriers. The Y cosubstitution is designed to counterbalance the Ca doping while maintaining the Bi concentration constant ($\text{Bi}_{2.5}\text{Ca}_x\text{Y}_{1-x}\text{Fe}_5\text{O}_{12}$ with $x = 0$ and 0.3) and sufficiently high, i.e., 2.5 Bi f.u.$^{-1}$ since Bi is known to govern the Faraday rotation intensity.$^{[15]}$

Doping solely with aliovalent cations was investigated previously on a parent compound, i.e., yttrium iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$, YIG). YIG is also a ferrimagnetic insulator (10$^{12}$ $\Omega$ cm at 300 K)$^{[16-18]}$ exhibiting a much weaker MO signal in the visible range than BIG and possessing most remarkably the lowest known magnetic damping.$^{[19]}$ Doped-YIG phases were usually synthesized.
either by applying the flux growth technique for single crystals or the liquid phase epitaxy (LPE) method for films thicker than 1 μm. Tetravalent cations such as Hf4⁺,[20] Sn4⁺,[21] and Si4⁺[22–24] were successfully substituted into the YIG lattice yielding n-type semiconductors with electrical resistivity values ranging from 10⁴ to 10⁵ Ω cm at room temperature. Conversely, divalent cationic substitutions such as Zn2⁺,[22] Mg2⁺,[25] Pb2⁺,[26] or Ca2⁺[22,24,25,27] in YIG yield p-type semiconductors with electrical resistivities ranging from 10² to 10³ Ω cm at 300 K; the best of them[27] being comparable to the n-doped YIG. For both n- and p-type YIGs, impurities such as Pb2⁺, F⁻, or B³⁺ (up to 0.1 f.u.) are unintentionally incorporated during the growth process. These defects act as extrinsic acceptors or donors that can partially account for differences in the electrical resistivity for a given carrier type and concentration. The presence of oxygen vacancies that can act as intrinsic donors in complex oxides also plays a key role in their transport properties. Oxygen concentration is directly linked to the growth conditions, but cationic substitutions can also influence the oxygen stoichiometry in a single oxide phase. In doped-YIG phases, it is known that the substitution of tetravalent cations prevents the presence of oxygen vacancies.[22,28] Conversely, divalent doping content favors the presence of oxygen vacancies in p-type YIGs that alter their electrical properties.[29] For instance, oxygen migration was further evidenced in p-type YIGs through annealing at T > 1100 K under inert/oxidizing atmosphere leading to small reversible resistivity changes (less than an order of magnitude).[22,28] Although thin films are ideal for integration into advanced nano-electronics, they are even more prone to defect inclusions than single crystals, and thus YIG-based thin films have been less widely investigated. However, 20 nm thick YIG films with a p-type conductivity of ≈10² Ω cm at 300 K were recently grown by LPE.[30] The authors suggest that this relatively low resistivity for undoped iron garnet originates either from the low dimensionality of the film or from the impurities incorporated during the growth process.

While the transport properties of YIG-based systems have been extensively studied and fine-tuned by appropriate cationic substitution and/or controlled atmosphere annealing, this proven approach has not yet been applied in the doped-BIG phases; only their structural, magnetic, and MO properties have been reported so far.[31–33] Here the electrical transport properties of Ca/Y-doped BIG thin films grown by pulsed laser deposition (PLD) onto gadolinium iron garnet (GGG) (001) substrates were investigated at room temperature and above, and further controlled under inert/oxidizing atmosphere to understand the influence of oxygen vacancies in the n-type Y-doped BIG phase. Electron energy-loss spectroscopy (EELS) performed in an aberration-corrected scanning transmission electron microscope (STEM) was used to map at the atomic scale the dopant distribution in the garnet lattice and to probe the charge compensation mechanisms in these thin films to furnish a better understanding of their electrical transport properties at the macroscopic scale.

### 2. Results and Discussion

The structural and MO properties of all our ≈180 nm thick Ca/Y-doped BIG films were first investigated. Undoped BIG, BiₓCaₓFe₂O₄₋ₓ (hereafter: B(Caₓ₀₀)IG), and Biₓ₂Caₓ₀.₅Feₓ₂O₁₂ (hereafter: B(Caₓ₀.₅)IG) thin films were grown on GGG (001) substrates by PLD. X-ray diffraction (XRD) patterns confirm that all films crystallize in the garnet structure (Figure S1, Supporting Information). A typical low-magnification bright-field TEM image of a doped BIG thin film (Figure S2a, Supporting Information) shows an epitaxial growth with the occurrence of secondary nonpercolating phases that are below the XRD detection threshold (Figure S2, Supporting Information). The doped thin films have slightly lower Faraday rotation values than pure BIG indicating preserved MO properties[34] in accordance with a lower Bi concentration.

Figure 1a presents the electrical transport properties measured at high temperatures (T > 300 K) under air atmosphere for BIG, B(Caₓ₀.₅)IG, and B(Caₓ₀.₅)IG films. The electrical resistivity values for all garnet films increase with decreasing temperature, indicating a semiconducting behavior (dp/dT < 0) with values of ρ(<450 K) = 8 × 10¹¹ Ω cm for BIG, ρ(<450 K) = 3.7 × 10¹¹ Ω cm for B(Caₓ₀.₅)IG, and ρ(<450 K) = 4.1 × 10¹¹ Ω cm for B(Caₓ₀.₅)IG. This represents a large improvement in the transport properties of iron garnet phases, with resistivities up to ten orders of magnitude lower than those of its parent compound, i.e., ρ(450 K) = 1 × 10¹¹ Ω cm for YIG.[16] These findings also confirm that doping BIG thin films with Ca/Y leads to an additional functionality exploiting their electrical conductivity. In particular, B(Caₓ₀.₅)IG films yield resistivity values as low as ρ = 9.6 × 10¹³ Ω cm at room temperature with an activation energy of Eₐ = 0.25 eV in between 300 and 400 K. The Seebeck coefficients as an intrinsic probe to determine the type of majority carriers were also measured in Ca/Y-doped BIG films. B(Caₓ₀.₅)IG presents a negative Seebeck coefficient with |S| around 15–25 µV K⁻¹ at 340 K (Figure S4, Supporting Information), indicating electrons as the predominant charge carriers with a concentration that can be estimated to 10²² – 10²³ cm⁻³ based on the Heikes formula.[35] Such carrier concentrations should lead to mobilities of ≈10⁻² – 10⁻¹ cm² V⁻¹ s⁻¹ which is somewhat too low for accurate Hall effect measurements. Among the n-type iron garnet systems, this B(Caₓ₀.₅)IG phase exhibits so far one of the lowest electrical resistivity values at 300 K, previously a comparable value has only been reported for an n-type Sn-doped YIG single crystal (10¹³ Ω cm at 300 K and Eₛ = 0.3 eV) in which additional charge carriers are introduced via tetravalent cationic substitutions.[21] Here, the transport properties of the n-type B(Caₓ₀.₅)IG phase appear to originate solely from the presence of oxygen vacancies acting as donors inducing Fe²⁺ as expressed in Equation (1)

\[
\text{Bi}_{1.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_{12.4} \rightarrow \text{Bi}_{1.5}\text{Ca}_{0.5}\text{Fe}_2\text{O}_{12.4} + 5\text{Fe}^{2+} + 12\text{O}_2^- \leftrightarrow (5-2\delta)\text{Fe}^{3+} + 2\delta\text{Fe}^{2+} + 2\delta\text{O}_2^- + \frac{\delta}{2}\text{O}_2 + (12-\delta)\text{O}_2^- \tag{1}
\]

The point defect equilibrium that describes the formation of oxygen vacancies in the n-type B(Caₓ₀₀)IG can be described using the Kröger–Vink notation[36] as

\[
5\text{Fe}^{3+} + 12\text{O}_2^- \leftrightarrow (5-2\delta)\text{Fe}^{3+} + 2\delta\text{Fe}^{2+} + 2\delta\text{O}_2^- + \frac{\delta}{2}\text{O}_2 + (12-\delta)\text{O}_2^- \tag{2}
\]
Fe$^{3+}$ and the Fe$^{2+}$ cation both at the Fe site. B(Ca$_{0.3}$Y$_{0.2}$)IG exhibits overall higher electrical resistivity values than the Y-doped films. The substitution of 0.3 Ca f.u. was chosen to match the dopant concentration of the best p-type YIG.$^{[27]}$ At that concentration, the electrical resistivity of B(Ca$_{0.3}$Y$_{0.2}$)IG could be measured only above 450 K due to its high impedance values and reaches almost $4 \times 10^3 \Omega \text{cm}$ at that temperature. B(Ca$_{0.3}$Y$_{0.2}$)IG films exhibit a large positive Seebeck coefficient with $|S|$ in the range of 300 µV K$^{-1}$ at 340 K (Figure S4, Supporting Information), indicating that holes are the predominant charge carriers with a concentration that can be estimated to $10^{19}$–$10^{20}$ cm$^{-3}$ using the Heikes formula.$^{[35]}$ This positive Seebeck coefficient is consistent with the Ca$^{2+}$ substitution acting as an acceptor that should induce the presence of Fe$^{4+}$ in B(Ca$_{0.3}$Y$_{0.2}$)IG. These resistivity values are one order of magnitude higher than those of the best Ca-doped YIG films obtained by LPE, i.e., around $10^2 \Omega \text{cm}$ resistivity at 450 K.$^{[27]}$ The difference might be due to a stronger self-compensation$^{[37]}$ of Ca$^{2+}$ with oxygen vacancies or a lower acceptor solubility in the thin films. The single scenario of the self-compensation mechanism can be written as followed:

$$\text{Bi}_{2}Y_{0.2}Ca_{0.3}Fe_{x}O_{12.8} \rightarrow \text{Bi}_{2}^{+}Y_{0.2}Ca_{0.3}^{+}Fe_{x}^{4+}Fe_{0.3-x}^{3+}O_{12.8}$$

which in the Kröger–Vink notation$^{[36]}$ becomes

$$0.3Ca^{2+}_{\text{in}} + 4.7Fe^{3+}_{\text{Fe}} + 0.3Fe^{2+}_{\text{Fe}} + 12O^{2-}_{\text{O}} \rightleftharpoons 0.3Ca^{3+}_{\text{in}} + (4.7 + 2\delta)Fe^{3+}_{\text{Fe}} + (0.3 - 2\delta)Fe^{2+}_{\text{Fe}} + 12O^{2-}_{\text{O}} + \delta V_{\text{O}}^\circ + \frac{\delta}{2}O_{(\delta)} + (12 - \delta)O_{(\delta)}^\circ \quad (\text{for} \ \delta < 0.15)$$

where $V_{\text{O}}^\circ$, Fe$^{3+}_{\text{Fe}}$, and Fe$^{2+}_{\text{Fe}}$, respectively, denote an oxygen vacancy with relative charge +2, the neutrally effective charged Fe$^{3+}$ and the Fe$^{2+}$ cation both at the Fe site. For both n-type B(Ca$_{0.0}$Y$_{0.5}$)IG and p-type B(Ca$_{0.3}$Y$_{0.2}$)IG thin films, oxygen vacancies as intrinsic donors appear to play a key role in the electrical transport properties as highlighted in Equations (2) and (4).

Hence, n-type B(Ca$_{0.0}$Y$_{0.5}$)IG films were further investigated under inert and oxidizing postannealing conditions in Figure 1b to understand the influence of the oxygen vacancies. Heating/cooling cycles (1 and 2 in Figure 1b) were applied first under N$_2$ atmosphere demonstrating that a low-resistance state (LRS) with $\rho(300 \text{ K}) = 10^3 \Omega \text{cm}$ is still preserved at 500 K. Heating under Ar atmosphere (3 in Figure 1b) keeps the B(Ca$_{0.3}$Y$_{0.2}$)IG films in the LRS until 600 K. However, thermal cycles under air above 500 K induces a transition to a high-resistance state (HRS) that remains when cooling down to room temperature with impedance larger than our measurement capabilities (>200 GΩ). This resistive change of at least three orders of magnitude is observed in Figure 1b.
of magnitude achieved under postannealing in inert/oxidizing atmospheres tends to confirm the key role of oxygen vacancies in the transport mechanisms as expressed in Equation (2) where the HRS state corresponds to the left side of the defect equilibrium, while the LRS state can be associated to the right one. The LRS and HRS are both stable in time at ambient temperature and pressure and XRD data confirm that the garnet phase is preserved in both states after thermal cycling as shown in Figure S5 (Supporting Information). Resistivity changes and their reversibilities were then examined further through subsequent cycles performed in different atmospheres. Figure 1c illustrates that the resistivity switch between the two states is totally reversible when alternating high-temperature annealing under inert/oxidizing atmospheres. This reversible resistivity change of large amplitude makes B(Ca0.0Y0.5)IG a promising material for gas sensing applications.

Analogous temperature cycles in inert/oxidizing atmospheres were performed for the p-type Ca-doped thin films. Here, no resistivity change was detected suggesting that a garnet lattice with low-level Ca substitution does not accommodate large oxygen stoichiometry variations.

Since, BIG-based systems with high bismuth concentration cannot be synthesized in bulk form, advanced local characterization methods based on electron spectromicroscopy techniques were performed to probe these nanostructures at the finest scale. Here, the B(Ca0.0Y0.5)IG and B(Ca0.3Y0.2)IG thin films are obtained by PLD. Hence the multication substitution may favor present structural and chemical defects and heterogeneities and dopants may not dissolve within the structure but rather form clusters. Oxygen vacancies might also be favored due to low-dimensionality effects (surface/interface proximity, strain effects, etc.). Such local modulations of the atomic and electronic structures strongly govern the physical properties of oxide thin films at macroscopic scale. The dopant solubility and charge compensation have therefore been investigated for both B(Ca0.0Y0.5)IG and B(Ca0.3Y0.2)IG by advanced spectromicroscopy techniques. Aberration-corrected (Cs) STEM/EELS, can probe core-loss absorption edges down to the atomic scale and is thus well suited to mapping the dopant distribution in the garnet lattice. At higher energy resolution, the local charge variations can be derived through the analysis of the spectral fine structures. The amount of Fe\(^{2+}\) (3d\(^6\)) can be identified by differences in Fe L\(_{2,3}\) fine structures with respect to Fe\(^{3+}\) (3d\(^5\)).\(^{[41]}\) Fe\(^{4+}\) has two spectral signatures; the main one is a prepeak on the O K edge because of the primarily 3d\(^3\)L nature of Fe\(^{4+}\), where L\(_1\) is a ligand hole, and another one on the Fe L\(_{2,3}\) edge as a result of its partial 3d\(^4\) nature.\(^{[42-44]}\)

The solubility of Y in the garnet matrix in the n-type B(Ca0.0Y0.5)IG is discussed first. Atomically resolved EELS chemical mapping was performed at the B(Ca0.0Y0.5)IG/GGG interface as shown in Figure 2. Elemental maps in Figure 2c,d,e show a homogeneous distribution of Y, Fe, and Bi, respectively, from the film/substrate interface, and up to 20 nm above. Figure 2g displays the normalized profiles of these maps, showing that the chemical interdiffusion at the interface is limited at most to the first 2 nm, i.e., less than two garnet unit cells and might be even narrower, since the Cs-STEM/EELS spatial resolution is limited by the probe broadening and the inelastic delocalization.\(^{[45]}\) In YIG/GGG systems, discrepancies were reported regarding the width of the chemical interdiffusion region, ranging from 2\(^{[46,47]}\) to 6 nm.\(^{[48]}\) Here, the B(Ca0.0Y0.5)IG/GGG interface thickness matches with the best of those results.

As the film/substrate interface is sharp and the cationic distribution is homogeneous, EELS core-loss fine structures were investigated at higher energy resolution in grains of B(Ca0.0Y0.5)IG over areas of a few hundred nm\(^2\) areas for each resistivity state, i.e., LRS and HRS. In LRS, oxygen vacancies are expected to induce Fe\(^{2+}\) which has a recognizable L\(_{2,3}\) edge spectral signature. Figure 3a,b displays Fe L\(_{3}\) and Fe L\(_{2}\) edges, respectively, probed in HRS and LRS films. While, the HRS system exhibits the typical fine structures of Fe\(^{3+}\) in a mixed Td and Oh environments as expected from an iron garnet structure.\(^{[41,49]}\) The LRS spectrum presents additional Fe\(^{2+}\) fine structures, highlighted by arrows in Figure 3a,b.\(^{[50]}\) The presence of Fe\(^{2+}\), Fe\(^{3+}\) and the clear signature of additional electrons that induce an increased n-type conductivity during inert atmosphere annealing, as expressed in Equation (2). To quantify the concentration of the induced charge carriers in the LRS relatively to the HRS, the LRS Fe L\(_3\) edge was fitted as a linear combination of siderite as an Fe\(^{2+}\) reference and the HRS as an internal Fe\(^{3+}\) reference using a least-square fitting method.\(^{[50-52]}\) The Fe site in siderite is solely in Oh coordination, and the LRS Fe\(^{2+}\) reference using a least-square fitting method. Figure 3c.\(^{[50-52]}\) The Fe site in siderite is solely in Oh coordination, and the LRS Fe\(^{2+}\) reference using a least-square fitting method. Figure 3c.\(^{[50-52]}\) The Fe site in siderite is solely in Oh coordination, and the LRS Fe\(^{2+}\) reference using a least-square fitting method. Figure 3c.\(^{[50-52]}\)
results in an Fe$	extsuperscript{2+}$/ΣFe ratio of 13 ± 1%, which corresponds to 0.65 Fe$	extsuperscript{2+}$ f.u.$^{-1}$, a δ = 0.325 based on Equation (2) and 2.6 × 10$^{21}$ cm$^{-3}$ electrons; corroborating further the carrier concentrations estimated from the Seebeck coefficient. In early work, concentrations of 0.07 Fe$	extsuperscript{2+}$ f.u.$^{-1}$ were reported in Sn$^{4+}$-doped YIG by means of chemical titration on flux grown samples.$^{[21]}$ Such a low Fe$	extsuperscript{2+}$ value might be attributed to the presence of impurities induced by the flux growth technique or the titration method that assumes no oxygen vacancies. More recently, in YIG ceramics, concentrations from 0.2 up to 1.25 Fe$	extsuperscript{2+}$ f.u.$^{-1}$$^{[49,53]}$ were determined by direct X-ray photoelectron and X-ray absorption spectroscopy techniques. The Fe$	extsuperscript{2+}$ concentration probed in the present work lies in the middle of the range of these reports. This indicates that the garnet structure might accommodate even more oxygen vacancies. Further annealing in inert atmosphere or higher levels of Y substitution might then induce a larger charge carrier concentration leading to an enhanced n-type conduction state.

The p-type B(Ca$_{0.3}$Y$_{0.2}$)IG exhibited an overall higher electrical resistivity than the n-type B(Ca$_{0.0}$Y$_{0.5}$)IG. The difference might originate from a lower acceptor solubility or a stronger self-compensation of Ca$^{2+}$ in the thin films as stated in Equation (4). The solubility of the Ca in the structure was first investigated by STEM/EELS. A Ca L$_{2,3}$ intensity map across a B(Ca$_{0.3}$Y$_{0.2}$)IG grain is shown in Figure 4b.

An oscillation of two percentage points in the Ca distribution was systematically observed at the nanometer scale along the growth direction. This feature has typically a pseudoperiod of 10–15 nm, i.e., 8–12 unit cells, and the Ca/Fe concentration ratio yields values between about 7.0% and 9.0%. The average Ca/Fe ratio over the film is around 8.0%, which is slightly higher than the value of 6.0% nominally expected during the PLD growth. To determine whether Ca substitutes within the garnet matrix, atomic-scale STEM/EELS was then performed in a Ca-rich region as shown in Figure 4d. The Ca L$_{2,3}$ and Fe

Figure 3. a,b) Sum of spectra of Fe L$_3$ and Fe L$_2$ edges, respectively, acquired with a 0.06 eV ch$^{-1}$ dispersion and a 100 ms exposure time on about a few hundred of nm$^2$ area in a grain of HRS (192 spectra, black dots) and LRS (756 spectra, orange squares). Characteristic Fe$^{2+}$ fine structures in LRS are indicated by black arrows. c) The LRS Fe-L3 edge was fitted from 706 to 712 eV as a linear combination (blue line) of the HRS spectral signature as Fe$^{3+}$ reference (orange line) and of the siderite as a Fe$^{2+}$ reference (green line).

Figure 4. a) HAADF intensity recorded simultaneously with the EELS map. b) Ca L$_{2,3}$ integrated intensity map. c) Summed profile of map (b). d) Atomically resolved HAADF survey image of B(Ca$_{0.3}$Y$_{0.2}$)IG acquired in a Ca-rich region. An atomic model of the garnet cation subcell of the garnet structure is overlaid on the HAADF image (Fe and Bi atoms are depicted in green and blue, respectively). e) Sum of 9 raw spectra of Ca L$_{2,3}$ and Fe L$_{2,3}$ edges probed in site 1 (red dotted line) and 2 (blue dotted line) in (d) are shown along with the normalized sum (black dotted line) of 14 160 spectra in this region. The energy dispersion used was 0.26 eV ch$^{-1}$ and each spectrum was acquired in 30 ms.
L$_{2,3}$ edges acquired over atomic columns 1 and 2 are displayed in Figure 4e. High-angle annular dark-field (HAADF) intensity scales roughly as $Z^{1.7}$ where $Z$ is the average atomic number of the probed atoms; Ca being a lighter element than Bi and Fe, it yields a less intense HAADF signal. A few atomic columns such as column 1, with up to 10% lower HAADF intensity than average, exhibit a higher Ca L$_{2,3}$ intensity which confirms that Ca is inserted into the BIG matrix and notably in a mixed Bi-Fe column. Differences in the Ca intensity between different atomic columns might be primarily of statistical origin (Figure S6, Supporting Information) and no obvious Ca clustering was observed. Since the Ca substitution in the BIG lattice yields nanometric Ca oscillations but no local Ca clusters, the charge compensation was further investigated in both Ca-rich and depleted regions at the nanometer scale and below to probe their respective electronic structures. When comparing column 1 to column 2, the latter presenting a lower Ca L$_{2,3}$ intensity (Figure 4e), no significant fine structure variation in the Fe L$_{2,3}$ edge (within the range of the present spectral resolution) was found indicating that the Fe-3d band population and the local Ca concentration are not spatially related. However, Ca$^{2+}$ substitution is expected to induce Fe$^{4+}$ states for which the strongest spectroscopic signature is a prepeak on the O K edge. Therefore, the evolution of the O K edge together with the Ca L$_{2,3}$ edge were probed in B(Ca$_{0.3}$Y$_{0.2}$)IG through the Ca oscillations along the growth direction.

In Figure 5b, the Ca L$_{2,3}$ edge intensity map shows a modulation similar to Figure 4b. Spectra from Ca-rich (A) and Ca-depleted (B) regions are shown in Figure 5d together with spectra acquired in BIG as a reference. A Ca-rich region is expected to induce locally more holes and therefore a higher intensity prepeak on the O K edge. However, the O K edges probed in regions A and B have the same fine structures as those of BIG; their edge onsets are at the same energy loss and none of these spectra exhibit any prepeak. One should note that probing low Fe$^{4+}$ densities by spectroscopy techniques is challenging because of the low O K cross-section and the mixed 3d$^6$/3d$^4$ natures of the Fe$^{4+}$ configuration. The quantification of holes in transition metal oxides by STEM/EELS has rarely reported and mostly in the case of a heavily hole-doped cuprates. In the present case, the low level of Fe$^{4+}$ concentration in the BIG lattice calls for higher energy resolution with high flux. Nevertheless, this absence of Fe$^{4+}$ signature, despite the solubility of ≈1.5% Ca in the garnet matrix, indicates that most of the Ca dopants do not introduce holes. This is consistent with the large positive Seebeck coefficient probed in B(Ca$_{0.3}$Y$_{0.2}$)IG and tends to corroborate the strong self-compensation of Ca$^{2+}$ by oxygen vacancies as described in Equation (4).

Both pure and doped BIG thin films present larger unit cells than their parent compound, i.e., YIG. This cell volume change may promote a decrease in the formation energy of oxygen vacancies in BIG systems resulting further in a stronger self-compensation of the divalent dopant. This trend is expected considering the known structural expansion caused by oxygen vacancies. Earlier works in TMO thin films reported on the strong cell volume and/or strain dependence linked to the oxygen vacancies formation where, for example, a tensile strain increases the concentration of oxygen vacancies in CaMnO$_3$. However, this effect is less pronounced in BIGs as demonstrated in the case of ZnO.

3. Conclusion

B(Ca$_{0.0}$Y$_{0.5}$)IG, B(Ca$_{0.0}$Y$_{0.2}$)IG, and BIG thin films retaining their state-of-the-art MO properties were grown on GGG substrates. They present semiconductor-like electrical resistivities as low as 10$^5$ Ω cm at room temperature for B(Ca$_{0.0}$Y$_{0.5}$)IG. Seebeck coefficient measurements revealed that B(Ca$_{0.0}$Y$_{0.5}$)IG exhibits n-type electrical transport with oxygen vacancies acting as donors, while B(Ca$_{0.0}$Y$_{0.2}$)IG presents p-type electrical transport with Ca$^{2+}$ acting as acceptors. In the former, an atmosphere-induced reversible resistivity change of three orders of magnitude was demonstrated. The origin of these properties was investigated by atomic-scale Cs-STEM/EELS techniques down to the atomic scale. Y, Bi, and Fe cations are distributed homogeneously in B(Ca$_{0.0}$Y$_{0.5}$)IG and chemical interdiffusion at the film/substrate interface is limited to the first 2 nm. A comparative fine structure study of Fe L$_{2,3}$ edges between the HRS and the LRS revealed the presence of 0.65 Fe$^{3+}$ f.u.$^{-1}$ in LRS that accounts for the increase in conductivity upon annealing.
under inert atmosphere. In contrast to $\text{Bi}([\text{Ca}_{0.0}\text{Y}_{0.3}])\text{IG}$, a pseudo-periodic inhomogeneity of 2% points magnitude in the Ca/Fe ratio along the growth direction was determined with a pseudoperiod of about 12 units cells in $\text{Bi}([\text{Ca}_{0.1}\text{Y}_{0.3}])\text{IG}$. However, Ca mapping down to the atomic scale tends to indicate that it is soluble within the BIG matrix. Advantage was taken of the Ca concentration heterogeneity at the nanometer scale to study the impact of Ca on the local density of states. No influence of Ca on either the Fe-3d or the O-2p bands structures was probed by EELS at the Fe L$_{3,3}$ and O K edges. Both this result and the solubility of Ca tend to show that oxygen vacancies self-compensate the holes as expressed in Equation (4) yielding high electrical resistivity in $\text{Bi}([\text{Ca}_{0.1}\text{Y}_{0.3}])\text{IG}$.

### 4. Experimental Section

$\text{Bi}_5\text{Fe}_5\text{O}_{12}$ (BIG), $\text{Bi}_5\text{Y}_{1.5}\text{Fe}_5\text{O}_{12}$ ($\text{Bi}([\text{Ca}_{0.0}\text{Y}_{0.5}])\text{IG}$), and $\text{Bi}_5\text{Ca}_{1.5}\text{Y}_{0.5}\text{Fe}_5\text{O}_{12}$ ($\text{Bi}([\text{Ca}_{0.1}\text{Y}_{0.3}])\text{IG}$) thin films of about 150 nm thick were grown by PLD onto GGG substrates. The BIG targets substituted with Ca and Y were prepared from high purity powders (99.99% for Ca precursor and 99.999% for all other precursors) using a standard ceramic processing method.$^{[5,6]}$ An excimer KrF laser with a wavelength of 248 nm and pulse duration of 20 ns was used for film deposition. The laser fluency and frequency were maintained at about 1.2 J cm$^{-2}$ and 2 Hz, respectively, for all the samples of the series. The films were grown onto (100) GGG heated to 1050 K under a stable oxygen pressure of 0.7 Pa. After the growth, the samples were cooled down in the growth atmosphere. $\text{Bi}([\text{Ca}_{0.0}\text{Y}_{0.5}])\text{IG}$ was postannealed for 96 h at 870 K under an O$_2$ flux of 50 mL min$^{-1}$. Faraday rotation measurements were carried out on a custom measurement setup described elsewhere.$^{[5] }$ The XRD data were acquired on a Seifert 4-circles X-ray diffractometer. GGG applies a compressive strain to the thin films and the lattice mismatch between them ranges from 1.6% to 2.3%. Circular Pt pads around 250 nm thick and 1 mm wide were deposited onto the film via RF-sputtering for ohmic contacts. The Pt pads were separated from each other by 2 mm from each other. Electrical resistivity measurements were performed following the classical four-probe van der Pauw method$^{[6]}$ in a custom-designed setup. With this setup, samples were able to measure with up to 200 GΩ internal impedance to directly determine the thermopower. Voltages at both hot and cold sides were measured using a Keithley 4200 SCS$^{[1]}$ controlled-temperature stage (Linkam Scientific Instruments Limited) over a temperature range of 300–700 K under ambient atmosphere or N$_2$/Ar flux of 1000–2000 mL min$^{-1}$. The Seebeck coefficients (S) were determined using another custom-designed experimental setup under ambient atmosphere. The temperature gradients $\Delta T$ were set using a RTD2 thermoregulator (Omicron technologies) with two heaters, separated by 6.5 mm from each other, placed below the substrate while voltage and temperature were both measured on the film surface above the heaters. $\Delta T$ were measured using two K-type thermocouples and reached positive or negative values between 5 and 30 K with $\pm$ 2 K fluctuations during voltage measurements. Voltages at both hot and cold sides were measured using a Keithley 4200 SCS of 10$^{11}$ Ω internal impedance to directly determine the thermopower as the ratio measurement of the sample voltage to the temperature difference. Cross-sectional electron-transparent samples were prepared by focused ion-beam (FIB) on a SCIOS dual-beam platform (FEI-Thermofischer) following the standard procedure. FIB lamellae were extracted from garnet films in both high- and low-resistance states. The electron spectromicroscopy experiments (STEM/EELS) were done on a Cs-corrected Nion UltraSTEM 200 operated at 100 kV with 30 mrad convergence angle, 50 mrad EELS collection angle, and around 50 pA of probe current. The microscope was equipped with a Gatan Enfina spectrometer with a custom high sensitivity camera. Different energy dispersions were used when acquiring EELS data. For Figure 2, the data were first denoised by principal component analysis (PCA)$^{[2]}$ using Hyperspy data-treatment software$^{[3]}$ and the first 6th components were kept (Figure S7, Supporting Information). The background was fitted with a power law on an energy window located before the edge and subtracted from the EELS spectra. The absorption edges were integrated over 60 eV for Gd M$_{4,5}$ and BiM$_{4,5}$ and over 20 eV for Fe L$_{2,3}$ and Y L$_{2,3}$. The Ca intensity map in Figure 4b was obtained the same way except that no PCA was applied and the Ca L$_{2,3}$ edge was integrated over 7 eV. To obtain Ca/Fe ratios, the intensities of the Ca L$_{2,3}$ and Fe L$_{2,3}$ edges were converted to relative atomic concentration using tabulated hydrogenic cross sections especially calculated for white lines over a 30 eV window.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

bismuth iron oxide, electron energy-loss spectroscopy, magnetic semiconductor, multifunctional single phase, pulsed laser deposition.

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