

# Multiferroism Induced by Spontaneous Structural Ordering in Antiferromagnetic Iron-Perovskites

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**ABSTRACT:** Room temperature multiferroism in polycrystalline antiferromagnetic Fe-perovskites is reported for the first time. In the perovskite-type oxides  $\text{RE}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  (RE = Gd, Tb) the interplay of layered ordering of the Gd(Tb), Ba and Ca atoms with the ordering of the  $\text{FeO}_4$ -tetrahedra (T) and  $\text{FeO}_6$ -octahedra (O) results in a polar crystal structure. The layered structure consists of the stacking sequence of RE/Ca-RE/Ca-Ba-RE/Ca layers in combination with TOOT sequence in a unit cell. A polar moment of  $33.0 \mu\text{C}/\text{cm}^2$  for the Gd-oxide ( $30.1 \mu\text{C}/\text{cm}^2$  for the Tb one) is determined from displacements of the cations, mainly Fe, and oxygen atoms along the b-axis. These oxides present antiferromagnetic ordering doubling the c-axis, the magnetic structure in the Tb-compound remains up to 690 K, which is one of the highest transition temperatures reported in Fe-perovskites.

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## INTRODUCTION

The interplay between compositional diversity and rich defect-chemistry within the  $\text{ABX}_3$  perovskite-structure designates it as a versatile framework to reach a wide array of functional properties<sup>1</sup>. Perovskites are among the most important families of complex oxides. Transition metal atoms usually occupy the B-positions of the structure, whereas alkaline, alkaline-earth and lanthanide atoms locate within the A-sites. Partial or total substitution of different A and B cations is a common strategy to modify and tune the properties of perovskite-oxides. In addition to the compositional flexibility, the perovskite structure presents structural flexibility to accommodate the different sizes and oxidation states of the A and B cations. Tilting of the octahedral network formed by the anion sublattice is the most frequent distortion for optimizing the matching between the A-O and B-O bond-distances<sup>2-4</sup>. This apparently simple distortion highly impacts on the bandwidth of the electronic structure and consequently determines the conducting and magnetic properties of the oxide<sup>5</sup>. Also the perovskite structure presents an outstanding ability to accommodate non-stoichiometry in the anion sublattice by creating anion vacancies. High concentration of anion vacancies originates different coordination polyhedral around the B-cations in addition to the  $\text{BO}_6$  octahedra. Besides, cation ordering of different atoms sharing the same A or B sites gives different superstructures based on the perovskite-type<sup>6</sup> having

astonishing influence on the properties of the “ordered compounds” compared to the disordered ones<sup>7,8</sup>. Therefore, by a thorough selection of the type of atoms in both the A and B sites of the structure, a wide combination of ordering effects and properties is opened in the perovskite oxides. For instance, the interplay between cation ordering, oxygen vacancies ordering and oxidation states of Cu determines the superconducting behavior in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ <sup>9</sup>; the location of the anion vacancies within the (GdO)-planes of the layered perovskite  $\text{GdBaCo}_2\text{O}_{5+\delta}$  plays an essential role in the conducting properties of this compound<sup>10</sup> and the combination of cation ordering with oxygen vacancy and charge orderings in  $\text{REBaMn}_2\text{O}_{5.75}$  (RE = Gd, Tb) determines its transport and magnetic properties<sup>11,12</sup>.

Materials or systems with co-existence of properties for achieving multifunctionality are extremely attractive. In this context, magnetoelectric multiferroic materials, which present co-existence of magnetic ordering and ferroelectricity, are among the most interesting from both the academic point of view and for applications<sup>13</sup>. In the case of perovskites, multiferroic behavior is not a trivial achievement, since these two properties seem to conceptually exclude one another<sup>14</sup>. Despite of this, there are ways to combine magnetism and ferroelectricity in perovskites such as in  $\text{BiFeO}_3$ , in which magnetic ordering is associated to the Fe but the Bi-lone-pair is responsible of the ferroelectric behavior<sup>15</sup>. Although ferromagnetism is usually the type of magnetic ordering occurring in magnetoelectric-

multiferroic perovskites, combination of ferroelectricity and antiferromagnetism has been predicted in the orthorhombic  $\text{BaMnO}_3$ <sup>16</sup> and in  $\text{YCaFe}_2\text{O}_5$ <sup>17</sup>. Layered-type ordering of different A-cations coupled with particular octahedral tilting systems of the anion sublattice results in non-centrosymmetric polar perovskites<sup>18,19</sup>. A more recent approach consisting of the combination of cation ordering with anion-vacancy ordering to generate polar structures has been demonstrated on epitaxially grown  $\text{SrFeO}_{2.5}/\text{CaFeO}_{2.5}$  thin-film superlattices<sup>20</sup>. The variety of coordination polyhedra that Fe can adopt makes this element ideal to promote coupling of cation and anion-vacancy orderings to form perovskite-based superstructures with different stoichiometry. Besides, stabilization of  $\text{Fe}^{3+}$  within the structure can provide strong super-exchange interactions to sustain magnetic ordering above room temperature, as for instance in  $\text{YBaFe}_2\text{O}_5$ <sup>21</sup>,  $\text{YFeO}_3$ <sup>22</sup> and  $\text{LaCa}_2\text{Fe}_3\text{O}_8$ <sup>23</sup>. The combination of these properties of iron can result in multiferroism, as it has been recently suggested for the layered-perovskite  $\text{YCaFe}_2\text{O}_5$ <sup>17</sup>. First-principle density functional theory calculations support strong polarization and robust magnetic ordering above room temperature in  $\text{YCaFe}_2\text{O}_5$ ; besides, the possibility of preparing this material by a layer-by-layer growth technique capable of imposing Y and Ca ordering has been suggested.

Taking into account these aspects, we report in this article the synthesis and characterization of the new room-temperature multiferroic oxides  $\text{RE}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  (RE = Gd, Tb) with perovskite-based crystal structure. These polycrystalline oxides present spontaneous layered-ordering of Gd(Tb), Ba and Ca atoms, which induces  $\text{FeO}_4$ -tetrahedra and  $\text{FeO}_6$ -octahedra ordering in a polar crystal structure. The crystal structure has been solved by means of advanced transmission electron microscopy techniques with atomic resolution. These oxides present antiferromagnetic ordering of  $\text{Fe}^{3+}$  up to 850 K, also showing both electric and magnetic phase transitions at the same temperature.

## EXPERIMENTAL METHODS

The initial composition of the compound to be subject of this study was  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5+\delta}$ , as part of the system  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Co}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$ .  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5+\delta}$  was synthesized by ceramic route using  $\text{Gd}_2\text{O}_3$  (Sigma Aldrich, 99.99%),  $\text{BaCO}_3$  (Sigma Aldrich, 99.99%),  $\text{CaCO}_3$  (Merck, 99.7%) and  $\text{Fe}_2\text{O}_3$  (Sigma Aldrich, 99.99%).  $\text{Gd}_2\text{O}_3$  was heated at 1173 K prior to weighing in order to avoid the  $\text{Gd}(\text{OH})_2$  contamination. Stoichiometric amounts of the starting materials were mixed and heated at 1173 K in air to decompose the carbonates. The sample was then pelletized and treated at 1473 K for 12 h with heating and cooling rates of 5 and 3 K  $\text{min}^{-1}$ , respectively. Subsequent cycles of regrinding and firing were performed in order to obtain single phase samples. The isostructural oxide  $\text{Tb}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5+\delta}$  was prepared using the same ceramic method as used for the Gd-compound with the aim of performing neutron diffraction experiments avoiding the strong neutron absorption of natural Gd.

The initial phase identification was carried out by Powder X-Ray Diffraction (PXRD) using the PANalytical X'PERT PRO MPD diffractometer with the  $\text{Cu K}\alpha_1$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) and X'PERT PEAPS software. The pattern was taken in step

mode with a step size of 0.017 (2 $\theta$  degrees) and acquisition time per step of 10 s. The average structure of the material was studied by Synchrotron X-Ray Diffraction (SXR) at the beamline BL02B2 of Spring-8 (Hyogo, Japan). A scan at 300 K was performed using radiation of 0.599748  $\text{Å}$  wavelength. The crystal structure parameters were refined by the Rietveld method using FullProf<sup>24</sup>. Besides, SXR patterns at different temperatures were taken in air in between 300 and 1050 K using a wavelength of 0.826560  $\text{Å}$  at TPS (Taiwan Photon Source) beamline 09A in NSRRC (National Synchrotron Radiation Research Center) in Hsinchu, Taiwan. A LeBail fitting (without a structural model) of the SXR patterns was performed to obtain the lattice parameters at the different temperatures.

Thermogravimetric (TG) analysis has been carried out in order to evaluate the oxygen stoichiometry of the compound from 300 K to 1173 K with heating and cooling rates of 5 K/min.

The nuclear and magnetic structures of the oxide  $\text{Tb}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5+\delta}$  were determined by neutron powder diffraction (NPD) on the D2B and D20 instruments at the ILL (Grenoble, France). High-resolution diffraction patterns were collected on D2B at 300 K and 1000 K using a wavelength  $\lambda = 1.594 \text{ \AA}$ . To determine the thermal evolution of the magnetic structure, patterns were collected between 300 K and 1000 K every 3.5 K on D20 with neutrons of  $\lambda = 2.41 \text{ \AA}$ , using a quartz tube open to air inside a furnace under vacuum. The data were fitted using FullProf<sup>24</sup>. Magnetic symmetry analysis was done using the program BASIREPS<sup>25,26</sup>.

High resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and Electron Energy-Loss-Spectroscopy (EELS) were performed with a JEOL JEM 3000F microscope operating at 300 kV (double tilt  $\pm 20^\circ$ ), fitted with a X-Ray energy dispersive spectroscopy (XEDS) microanalysis system (OXFORD INCA) and ENFINA spectrometer with an energy resolution of 1.2 eV. The atomic ratio of the metals of the oxide was determined by XEDS analyses, showing good agreement between analytical and nominal composition in all the crystals. Average oxidation state of Fe cations was determined by EELS. The spectra were acquired in diffraction mode, with a dispersion of 0.1 eV/channel, a collection angle of  $\beta \sim 5.4 \text{ mrad}$  and an acquisition time of 1.5 s. A power-law model was used to remove the background of the spectra.

High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) analyses were performed on an ARM200cF microscope, fitted with a condenser lens aberration corrector (point resolution in STEM mode of 0.08 nm). HAADF images were acquired with an inner acceptance angle of 90 mrad and ABF ones with a collection angle of 11 mrad. The same ARM200cF microscope was employed for EELS experiments, since it is fitted with a GIF Quantum-ER spectrometer. EELS mapping was performed with a collection semi-angle  $\beta \sim 30 \text{ mrad}$ , dispersion energy of 0.5 eV/channel and collection time for each spectrum of 0.09 seconds. Gd-M<sub>4,5</sub>, Fe-L<sub>2,3</sub>, Ba-M<sub>4,5</sub> and Ca-L<sub>2,3</sub> edge signals were chosen for mapping.

<sup>57</sup>Fe Mössbauer spectra were measured to confirm the oxidation states and oxygen environments for the Fe cations,

and to study the magnetic states in the compound. The measurement was performed at room temperature in transmission geometry with a constant-acceleration spectrometer using a  $^{57}\text{Co}/\text{Rh}$  radiation source. The velocity scale and the isomer shift (IS) were determined with the relative values of  $\alpha\text{-Fe}$  at room temperature. The spectrum was fitted to Lorentzian functions by using the standard least-squares method.

The Magnetic properties of the compound were measured by CS-3 Furnace Apparatus at 5 Oe in the temperature range in between 300 K and 950 K.

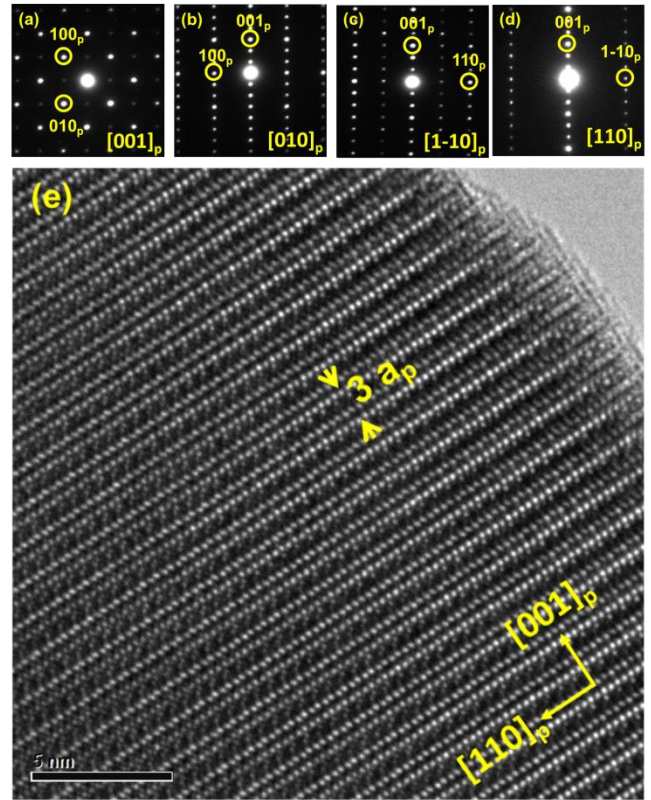
Electrical conductivity was determined by a d.c. four probe method on rectangular bars in the range between 300 and 1200 K using a potentiostat/galvanostat equipment (Autolab PGSTAT302N) in a galvanostatic mode.

## RESULTS AND DISCUSSION

### Structural characterization

The initial composition of one of the compounds to be subject of this study was  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5+\delta}$ , as part of the system  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Co}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$ . The PXRD pattern of the sample with composition  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5+\delta}$  is characteristic of a single-phase material with perovskite-related structure (**Supporting Information, Figure S1**). A weak low-angle reflection appears at  $2\theta \sim 7.5^\circ$ , which corresponds to an interplanar distance  $d_{\text{hkl}} \sim 11.3 \text{ \AA}$  reflecting, in principle, a three-fold superstructure. The average oxidation state of Fe in the present compound, close to  $3+$  ( $2.91 \pm 0.04$ ), has been determined from the L3/L2 intensity ratio of the Fe-L<sub>2,3</sub> ionization edge of several EELS spectra (**Supporting Information, Figure S2**). Taking into account this oxidation state of Fe found by EELS and that the XEDS analysis confirmed the nominal cation composition of the oxide, one can determine the oxygen content to  $\delta = 0.33$ , which agrees with the stoichiometric formula  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ .

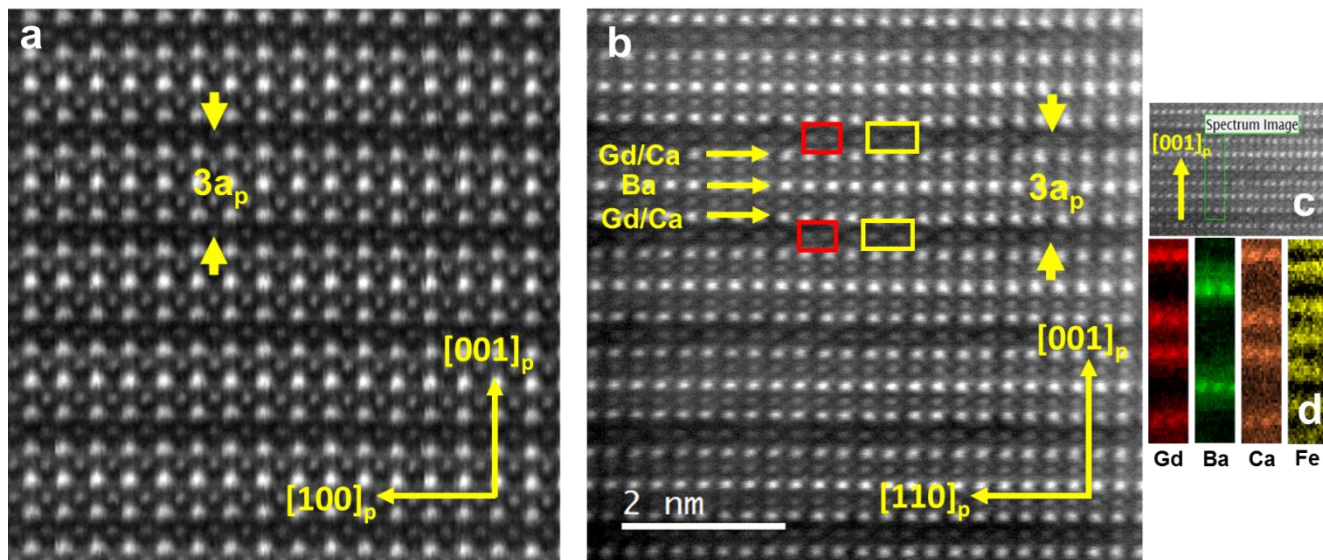
Further investigations of the crystal structure have been performed by SAED and HRTEM analyses. **Figure 1** shows SAED patterns along different zone axes of a crystal of the compound. All the patterns have been indexed according to the cubic perovskite structure. The pattern along the  $[001]_p$  zone axis shows the characteristic reflections of the cubic perovskite and weak extra reflections at  $G_p \pm 1/2 (110)_p^*$  associated with the formation of the so-called diagonal cell ( $\sqrt{2}a_p \times \sqrt{2}b_p$ ) within the  $ab$  plane. Moreover, in the SAED pattern along the  $[010]_p$  zone axis, strong extra reflections at  $G_p \pm 1/3 (001)_p^*$  appear, revealing the three-fold superstructure along the stacking axis. Both types of the above mentioned extra reflections at  $G_p \pm 1/2 (110)_p^*$  and  $G_p \pm 1/3 (001)_p^*$  appear in the SAED pattern along the  $[1-10]_p$  zone axis but only the  $G_p \pm 1/3 (001)_p^*$  in the  $[110]_p$  one. Therefore, a  $\sqrt{2}a_p \times \sqrt{2}b_p \times 3c_p$  unit cell is concluded by construction of the reciprocal lattice from the SAED patterns of the  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  oxide. **Figure 1d** shows the HRTEM image along the  $[1-10]_p$  zone axis. Contrast differences characteristic of the  $3a_p$  periodicity along the  $[001]_p$  direction are observed in the whole crystal without domains with different crystal microstructure. All the crystals studied present long-range modulation in their crystal structure.



**Figure 1.** Experimental SAED patterns of a crystal of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  along the (a)  $[001]_p$ , (b)  $[010]_p$ , (c)  $[1-10]_p$  and (d)  $[110]_p$  zone axes. The patterns have been indexed on the basis of a cubic perovskite structure. (e) Experimental HRTEM image of the crystal along the  $[1-10]_p$  zone axis.

HAADF-STEM images (Z contrast images) in combination with EELS mapping give information about the cation arrangement within the structure with atomic resolution, which in addition to the information provided by SAED and HRTEM allows to solving the crystal structure of the compound. **Figure 2a** and **b** shows HAADF-STEM images along the  $[010]_p$  and  $[1-10]_p$  zone axes of a crystal of  $\text{RE}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ .



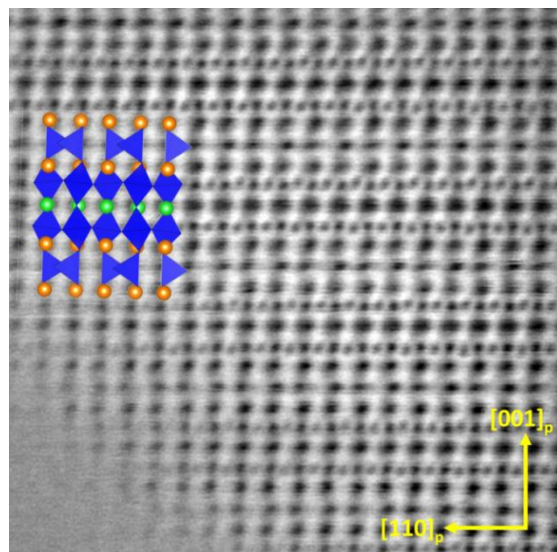


**Figure 2.** Experimental HAADF-STEM images of a crystal of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  along the (a)  $[010]_p$ , (b) and (c)  $[1-10]_p$  zone axes, and (d) EELS maps of the area of the crystal indicated in green in (c). Columns of Gd atoms are indicated in red, Ba atoms in green, Ca atoms in brown and Fe atoms in yellow. Two Fe-Fe distances (0.34 and 0.24 nm) along  $[110]_p$  direction are indicated with yellow and red frames respectively

The contrast differences in the images confirm the  $3a_p$  superstructure along the  $[001]_p$  direction as due to A-cation ordering. The EELS mapping (**Figure 2d**) reveals the layered-type ordering of the A-cations as a sequence of two consecutive layers containing both Gd and Ca atoms alternated with one layer of Ba atoms (i.e. Gd/Ca - Gd/Ca - Ba - Gd/Ca sequence). In addition to the contrast associated to layered-ordering of the A-cations, the layers of columns of Fe atoms located between the two layers of columns containing Gd and Ca show weaker contrast than the layers of columns of Fe atoms located between one layer of columns of Ba atoms and one containing Gd and Ca.

This weaker contrast seems to be associated with a lower anion-coordination of the Fe atoms in those positions. Moreover, the image of the  $[-110]_p$  zone axis reveals that these Fe-layers present two clearly different Fe-Fe distances (0.34 and 0.24 nm) alternating along the  $[110]_p$  direction (indicated in the figure by yellow and red frames). In order to visualize the anion sublattice, ABF-STEM experiments have been carried out. **Figure 3** shows the ABF-STEM image of a crystal of the compound along the  $[-110]_p$  zone axis. Both the ABF-STEM image and the corresponding HAADF-STEM image along the  $[-110]_p$  zone axis are also shown in **Supporting Information, Figure S3** for comparison. The columns of oxygen atoms are indicated in yellow. Two different oxygen environments around the Fe cations are clearly distinguished: the diffuse contrast associated to the oxygen atoms in the Fe-O layer in between layers containing Gd and Ca indicates a low, probably, four oxygen-coordination of Fe (Fe in oxygen-tetrahedral polyhedron); in the other two Fe-O layers of the unit cell, the two columns of oxygen atoms besides the Fe-atom-columns are clearly viewed, indicating Fe located in octahedral coordination. The stacking sequence along the  $[001]_p$  direction of the Fe-coordination polyhedra results in an Tetrahedra-Octahedra-Octahedra-Tetrahedra (T-O-O-T) ordering. The image also reveals a slight tilting of the oxygen-octahedra as a consequence of shifting of the oxygen atoms of the Fe-O layers towards the Gd/Ca-O layers.

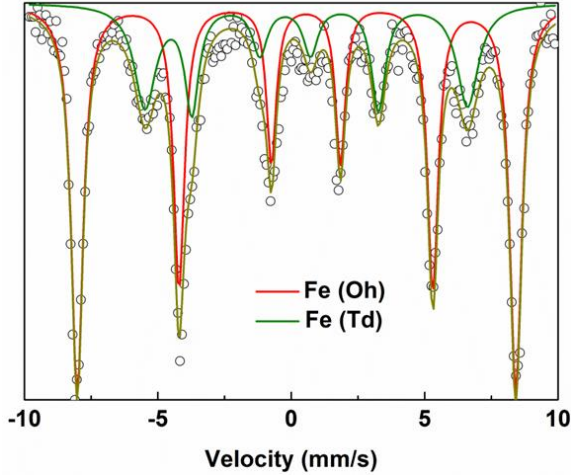
In summary, the transmission electron microscopy analyses conclude that the  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  oxide presents a layered-type perovskite structure with a  $\sqrt{2}a_p \times \sqrt{2}b_p \times 3c_p$  unit cell related to the layered-ordering of A-cations in a Gd/Ca-Gd/Ca-Ba-Gd/Ca sequence with a combined T-O-O-T ordering sequence of the Fe-O polyhedra. Lower magnification images of different crystals clearly show a long range formation of this perovskite-superstructure.



**Figure 3.** Experimental ABF-STEM image of a crystal of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  along the  $[-110]_p$  zone axis. Green spheres mark columns of Ba atoms, orange spheres mark columns of Gd/Ca atoms and coordination polyhedra around Fe atoms are indicated in blue.

Mössbauer analysis performed at room temperature (**Figure 4**) reveals a complex spectrum that consists of two different components in an area ratio 2:1 with Isomer Shifts (ISs) of 0.37 mm/sec and 0.17 mm/sec, and quadrupolar

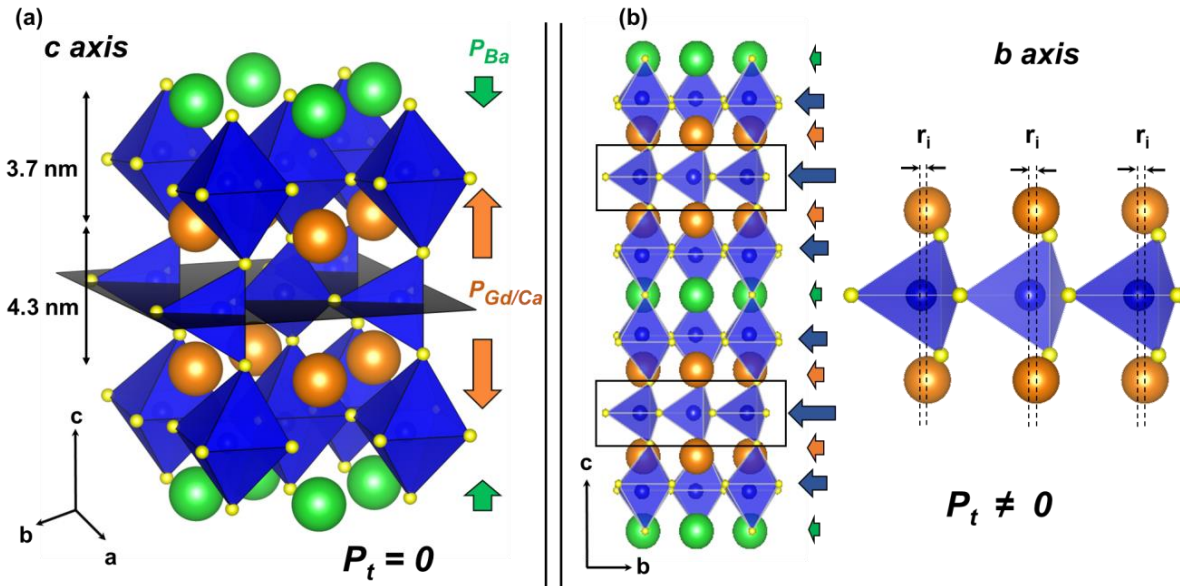
splittings (QSS) of -0.36 mm/sec and 0.79 mm/sec, respectively. These different ISS and QSS are attributed to the two different Fe<sup>3+</sup> sites (in octahedral and tetrahedral coordination) as determined by structural analysis consistent with the Mössbauer area ratio. Moreover, both Fe components are split into six lines indicating magnetic ordering of the Fe within the crystal structure with hyperfine parameters (HF) of 50 and 37 T for octahedral and tetrahedral sites, respectively.



**Figure 4.** Mössbauer spectra of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  at room temperature. The dots show experimental data and the lines show the Lorentzian fits. Red line marks the peaks for Fe in octahedral sites and green line marks the peaks for Fe in tetrahedral sites.

With the aim of refining the crystal structure concluded from the SAED, HRTEM and STEM results, SXRD measurements at room temperature have been performed. The space group has been determined from the following reflection extinctions  $0kl: k = 2n+1$  and  $0k0: k = 2n+1$ , which have been deduced by the construction of the reciprocal lattice from the SAED patterns (the pattern of the  $[001]_p$  zone axis shows double diffraction). These reflection extinctions correspond to the extinction  $\text{Pb}^-$  group, which allows the space groups  $\text{Pb}2_1\text{m}$ ,  $\text{Pbm}2$  and  $\text{Pbmm}$ . However, the space groups,  $\text{Pbm}2$  and  $\text{Pbmm}$  can be discarded since give a multiplicity of the sites that needs the splitting of the position of some atoms in the structural model inferred by STEM analyses. Therefore  $\text{Pb}2_1\text{m}$  is the space group of the crystal structure of this compound. These space group and unit cell are in agreement with three-fold perovskite-superstructures found in other Fe-oxides<sup>23,27</sup>.  $\text{Pb}2_1\text{m}$  lacks inversion center leading to a possible polarization along the b-direction. Results of the crystal structure refinement (**Supporting Information, Figure S4 and Table S1**) confirm the deduced  $\sqrt{2}a_p \times \sqrt{2}b_p \times 3c_p$  unit cell with orthorhombic  $\text{Pb}2_1\text{m}$  space group and the threefold layered ordering of the Gd, Ba and Ca atoms. Despite the EELS mapping of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  concludes that the Ba atoms are located in a single (001)-layer, the composition of this oxide, in agreement with the nominal one according to the XEDS results, indicates that a small concentration of Ba atoms should be located within the Gd/Ca layers. In fact, in the refinement of the crystal structure a 10% of Ba-atoms in the 4c crystallographic positions have been considered.

Recalling that  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5.33}$  ( $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ ) represents one end member of the solid solution  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Co}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$  the above detailed structural analysis permits to make a first remark concerning the change from a  $10a_p$  to a  $3a_p$  perovskite superstructure as Co is completely substituted by Fe while maintaining the Gd, Ba, Ca ratio<sup>28</sup>. This structural change is probably related to the suppression of the isolated Gd-O layers, which are present in the case of  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Co}_{1.6}\text{Fe}_{0.4}\text{O}_{5.41}$ . These Gd-O layers concentrate oxygen vacancies avoiding the formation of the tetrahedral anion environments around the Fe/Co cations. In  $\text{Gd}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Co}_{1.6}\text{Fe}_{0.4}\text{O}_{5.41}$ , the stacking sequence of the different A-O layers (Gd/Ca-Gd/Ca-Ba-Gd-Ba-Gd/Ca) contains one isolated Gd-O layer resulting in a  $5a_p$  periodicity. To accommodate the oxygen content, and taking into account that the Gd-O planes stabilize the location of anion vacancies, the stacking sequence of the coordination polyhedral around the Co/Fe atoms is T-O- $\text{O}_v$ - $\text{O}_v$ -O-T ( $\text{O}_v$  denotes oxygen-octahedra containing oxygen vacancies located within the Gd-O layers) along the same direction than the layered A-cation ordering (the different orientation of the two consecutive T-layers originates the  $10a_p$  periodicity). The greater capability of the Fe cations compared to the Co ones to be surrounded by tetrahedral anion polyhedra might be the reason for increasing the number of T-layers per unit cell leading to the stoichiometric  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  and also for driving a different ordering-sequence in the A-cation sublattice, without isolated Gd-O layers that could capture anion vacancies. A further interesting structural feature found in  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  is the singular stacking sequence of the A-cations. Two other Fe oxides with general formula  $\text{YBa}_2\text{Fe}_3\text{O}_8$ <sup>29</sup> and  $\text{LaCa}_2\text{Fe}_3\text{O}_8$ <sup>23</sup> and with a  $3a_p$  superstructure have been previously reported. Despite presenting  $\text{AE}^{2+}$ -  $\text{AE}^{2+}$ -  $\text{RE}^{3+}$  -  $\text{AE}^{2+}$  (AE: Alkaline Earth and RE: Rare Earth) ordering giving the same threefold modulation, the Fe-coordination sequence differs in these two compounds. While in  $\text{YBa}_2\text{Fe}_3\text{O}_8$ , the  $\text{Y}^{3+}$  layers create two square-based pyramidal polyhedra around Fe (O-SP-SP-O stacking sequence),  $\text{LaCa}_2\text{Fe}_3\text{O}_8$  presents only one Fe-layer in tetrahedral environment in between the two consecutive  $\text{Ca}^{2+}$  layers (T-O-O-T stacking sequence), like in  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ . However,  $\text{LaCa}_2\text{Fe}_3\text{O}_8$  and  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  differ in the cation distribution within the A-sublattice. Therefore,  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  presents a novel stacking sequence of the A-cations where the  $\text{RE}^{3+}$  layers are adjacent to the T layers.



**Figure 5.** Graphic representation of the polar unit cell of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ . (a) Arrows indicate polarization due to Ba atoms (green) and Gd/Ca atoms (orange) displacements along the  $c$ -axis. The length of the arrows is proportional to  $P$ . The  $m$  plane perpendicular to the  $c$  axis (represented in grey) cancels out  $P_t$ . (b) Arrows indicate polarization in the different layers (Ba-O layers in green, Gd/Ca-O in orange, Fe-O in octahedral layers and Fe-O in tetrahedral layers) including the anionic and cationic contributions along the  $b$ -axis.  $r_i$  is the shift-distance of the Fe atoms with respect to the A cations along the  $b$ -axis.

The cell parameters of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  undergo a non-isotropic linear expansion upon heating without showing any discontinuity according to the Le-Bail fitting of the PXRD patterns up to 1000K (**Supporting Information, Figure S5**). The linear expansion of the unit cell suggests a fixed oxygen content from room temperature to 1000 K, as it was confirmed by TG analysis in air, which shows no weight variations outside of the error range of the measurement (**Supporting Information, Figure S6**).

#### Polar properties

The polar space group  $\text{Pb}2_1\text{m}$  of the  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  oxide admits the existence of a net polarization from uncompensated shifts of the cations within the structure.

The polarization  $P$  can be calculated from the Rietveld refinement results using the following equation:

$$P = \frac{C}{\Omega} \sum_i q_i r_i$$

where  $C$  is the Coulomb constant,  $\Omega$  is the unit cell volume,  $q_i$  is the charge of the  $i$  cation and  $r_i$  the shifting of the  $i$  cation with respect to the theoretical centrosymmetric structure.

The alternating Ba and Gd/Ca layers exhibit antipolar displacements from their ideal positions along the  $c$  axis. The displacement of the Ba atoms is lower than the one of the Gd and Ca atoms resulting, in principle, in a total polarization, as shown in **Figure 5a**. However, the presence of the mirror plane  $m$  perpendicular to the  $c$  axis cancels out this polarization, contrary to the situation observed in the epitaxially grown  $\text{SrFeO}_{2.5}/\text{CaFeO}_{2.5}$  thin-film superlattices<sup>20</sup>.

On the contrary, all the tetrahedrally coordinated Fe atoms are shifted in the same direction along the  $b$ -axis creating polarization, as shown in **Figure 5b**. The polar space group  $\text{Pb}2_1\text{m}$  allows the tetrahedral layers to have the same

handedness (left handed in the **Figure 5**) within the entire structure creating an in-plane polarization. Besides, not only the Fe cations in a tetrahedral environment but all the atoms within the structure are shifted from their theoretical positions in the non-distorted structure contributing to the net polarization. Taking into account both the anion and cation shifts and assuming the middle point of the distance between consecutive Ba cations in the layer as the reference point for calculating the shifts of the atoms, the resulting polarization is  $33.0 \mu\text{C}/\text{cm}^2$  along the  $b$ -axis (note that the polarization has been calculated from the SXRD results, which do not give precise values of the oxygen coordinates).

#### Magnetic and electron-transport properties

The room temperature M-H variation (**Supporting Information, Figure S7**) is linear up to 5 T and has no remanence or coercivity, suggesting an antiferromagnetic-type (AFM) ordering of the  $\text{Fe}^{3+}$  ( $d^5$ , HS,  $S = 5/2$ ) within the structure. The temperature dependence of the magnetic susceptibility under a magnetic field of 5 Oe in the range between 300 and 1000 K, shown in **Figure 6a**, sets the AFM ordering temperature well above room temperature.

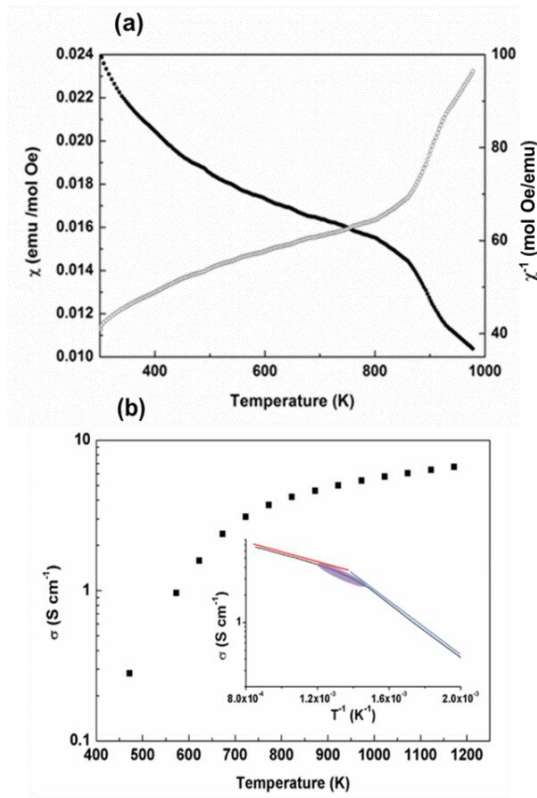


**Table 1.** Results of the Rietveld Refinement of the crystal structure of  $\text{Tb}_{0.8}\text{Ba}_{0.8}\text{Ca}_{0.4}\text{Fe}_2\text{O}_{5.33}$  from NPD data at room temperature. The y position of Ba has been fixed, since it has been taken as reference point for calculating the polarization of the cell.

Atom	Site	x	Y	Z	B <sub>iso</sub>	Occupancy
Ba	2a	0.265(2)	0.75	0.0	0.9(1)	1
Tb/Ca/Ba	4c	0.261(1)	0.743(1)	0.3154(4)	1.07(8)	0.548(2)/0.350(2)/0.103(2)
Fe (Oh)	4c	0.2467(9)	0.246(3)	0.1692(2)	0.86(4)	1
Fe (Td)	2b	0.2072(9)	0.224(3)	0.5	0.86(4)	1
O1	4c	0.001(3)	0.003(3)	0.2001(4)	0.98(4)	1
O2	4c	0.499(3)	0.011(4)	0.1731(5)	0.98(4)	1
O3	2b	0.129(2)	0.859(4)	0.5000	0.98(4)	1
O4	2a	0.234(2)	0.262(4)	0.0	0.98(4)	1
O5	4c	0.307(1)	0.280(4)	0.3572(3)	0.98(4)	1

$$a = 5.5721(1), b = 5.5173(1), c = 11.5786(3)$$

$$R_{wp} = 4.69 \%, R_p = 3.59 \%, R_{exp} = 1.76 \%, R_B = 6.66 \%, \chi^2 = 7.12$$



**Figure 6.** (a) Temperature dependence of the magnetic susceptibility of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  within the range between 300 K and 1000 K. (b) Total dc conductivity as a function of temperature of  $\text{Gd}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ . The inset depicts the Arrhenius dependence of the conductivity with the temperature with two different regimes shown in red and blue. The purple zone is indicating the extension of the intermediate region.

The inverse of the magnetic susceptibility deviates from the linearity at  $T = 850$  K indicating magnetic ordering of the Fe below this temperature without any change in the oxidation state of Fe according to the TG analysis.

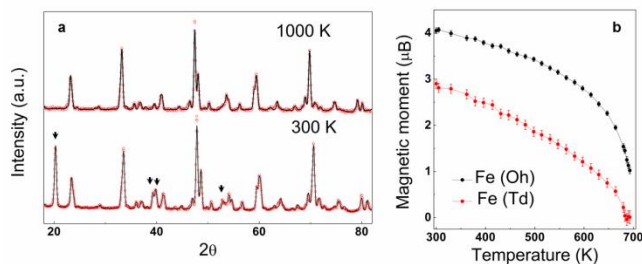
Besides, the variation of the electrical resistance of the oxide as a function of temperature (**Figure 6b**) reveals two linear trends between 450-1200K with a change in the slope, which should be associated with the magnetic ordering. This change cannot be related to a modification in the oxidation state of the Fe because, according to the TGA, the oxygen content remains constant in this temperature regime. A semiconducting behavior is observed over the whole range of temperatures with two different regimes below  $\sim 700$  K and above  $\sim 890$  K with activation energies  $E_a = 288$  and  $112$  meV, respectively.

It seems that there is not an electrical transition at a particular temperature but the change of regime takes place in a range of 150 K, which evidences some anomalies in the magnetic behavior of this compound (the magnetic transition occurs at about 850 K). This close relation between electronic conductivity and magnetic behavior is observed in other  $\text{Fe}^{3+}$  containing compounds such as  $\text{Ca}_2\text{Fe}_2\text{O}_5$ <sup>30</sup> and  $\text{NdFeO}_3$ <sup>31</sup>, in which the spin alignment via superexchange ( $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ ) localizes the electrons increasing the electrical  $E_a$ .

#### Magnetic structure

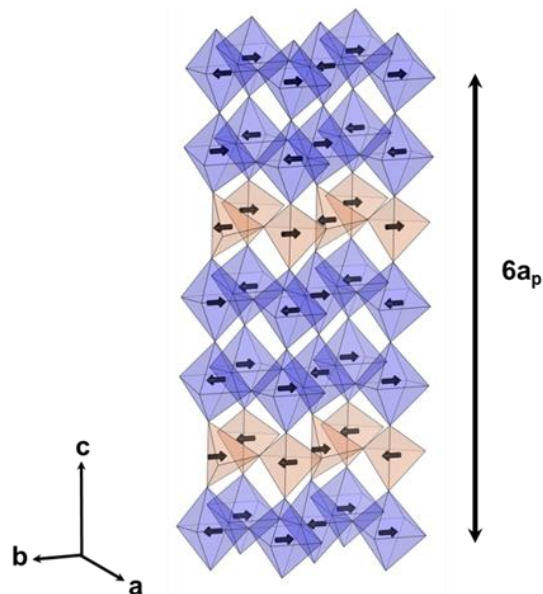
PND patterns collected between 300 K and 1000 K were used to determine the magnetic structure of the compound replacing  $\text{Tb}^{3+}$  by  $\text{Gd}^{3+}$  due to the high absorption of this latter cation. The replacement of Gd by Tb maintains the nuclear structure according to the PND data refinement (**Table 1** in the main text and in **Supporting Information, Table S2**) and the antiferromagnetic ordering, although the paramagnetic behavior differs probably due to the different

contribution of the  $\text{Tb}^{3+}$  to the total magnetic moment (**Supporting Information, Figure S8**). The Tb-oxide also presents a polar moment of  $23.2 \mu\text{C}/\text{cm}^2$  along the b-axis. Magnetic reflections in the PND patterns of  $\text{Tb}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  appear below 700 K. The magnetic reflections can be indexed by a propagation vector  $[0\ 0\ \frac{1}{2}]$  as it is shown in **Figure 7a**, producing a magnetic unit cell  $\sqrt{2}a_p \times \sqrt{2}b_p \times 6c_p$ . Magnetic symmetry analysis was used to determine the allowed irreducible representations and their basis vectors for the  $\text{Fe}^{3+}$ -site and are included in **Supporting Information, Table S3**. The magnetic structure adopted below 700 K is presented in **Figure 8**. It consists of a three dimensional G-type antiferromagnetically ordered arrangement of the Fe spins with the spin directions lying along the b axis. At room temperature two different magnetic moments of  $4.04(9) \mu\text{B}$  and  $3.1(2) \mu\text{B}$  for the Fe in octahedral and tetrahedral sites respectively are determined, both lower than the theoretical value of  $5 \mu\text{B}$ . This fact can be explained by the lowering of the magnetic moment associated with the thermal spin fluctuations. As it is shown in **Figure 7b**, the magnetic moment of the Fe in both sites follows a characteristic Brillouin curve. Moreover, the lower magnetic moment can furthermore be associated with a non-purely ionic bonding between Fe and O. The covalence degree, more marked in the tetrahedral sites, induces the transfer of some magnetic moment to the O atoms decreasing the magnetic moment.



**Figure 7.** (a) PND patterns of  $\text{Tb}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  taken below (300 K) and above (1000 K) the magnetic transition. The arrows indicate the magnetic reflections. (b) Temperature dependence of the magnetic moment of Fe in the octahedral (black) and tetrahedral (red) sites of  $\text{Tb}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ .

The long range antiferromagnetic structure extends up to  $\sim 690$  K. Above this temperature short range magnetic order is still visible up to about 800 K in the neutron diffraction data of D2O as a broad contribution. This short-range ordering mirrors the presence of magnetic interactions of Fe up to  $\sim 850$  K according to the magnetic measurements, as already found in  $\text{Ca}_2\text{FeMnO}_5$ <sup>32</sup>.



**Figure 8.** Magnetic unit cell of  $\text{Tb}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$ . Arrows indicate the spin direction.

## CONCLUSIONS

As conclusion, room temperature multiferroism in polycrystalline antiferromagnetic Fe-perovskites is reported for the first time. These perovskite-type oxides with composition  $\text{RE}_{1.2}\text{Ba}_{1.2}\text{Ca}_{0.6}\text{Fe}_3\text{O}_8$  (RE = Gd, Tb) have been prepared by ceramic method. The interplay of layered ordering of the Gd(Tb), Ba and Ca atoms with the ordering of the  $\text{FeO}_4$ -tetrahedra (T) and  $\text{FeO}_6$ -octahedra (O) results in a orthorhombic polar crystal structure with non-centrosymmetric  $\text{Pb}2_1\text{m}$  space group. The layered structure consists of the stacking sequence of RE/Ca-RE/Ca-Ba-RE/Ca layers in combination with TOOT layers in a  $\sqrt{2}a_p \times \sqrt{2}b_p \times 3c_p$  unit cell. A polar moment of  $33.0 \mu\text{C}/\text{cm}^2$  for the Gd-oxide ( $23.2 \mu\text{C}/\text{cm}^2$  for the Tb one) is determined from displacements of the cations, mainly Fe, and oxygen atoms along the b-axis. These oxides present antiferromagnetic ordering in a  $\sqrt{2}a_p \times \sqrt{2}b_p \times 6c_p$  magnetic unit cell, determined in the Tb-compound. Antiferromagnetic ordering is maintained up to 690 K, which is one of the highest transition temperatures reported in Fe-perovskites. The magnetic transition is associated to an electric transition of electron transport at the same temperature. Although these results open new perspectives to multifunctionality in perovskites, the magnetoelectric coupling of the ferroic properties would be essential for some applications. In this sense, studies of electric-field control of magnetism or electric polarization under magnetic fields are interesting to be carried out in these Fe-perovskites.

## ASSOCIATED CONTENT

### Supporting Information.

PXRD patterns, EELS spectrum, HAADF-STEM and ABF-STEM images, refined crystal structure parameters, lattice parameters vs T, TGA, M vs H,  $\chi$  and  $\chi^{-1}$  vs T and irreducible representations and basis vectors of Fe in the magnetic structure.

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