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A Series of Novel Mixed Valent Ferrimagnetic Oxides with a T_C up to 270 K: $Ca_{1-x}Y_xBaFe_4O_7$

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Numerous studies of strongly correlated electron oxides have shown that the mixed valence of the transition element is a very important factor governing the magnetic and transport properties of these materials. In most of them, the coordination of the transition element is octahedral or pyramidal, as shown for superconductive cuprates and magnetoresistive manganites and cobaltites, with structures closely related to the perovskite. In contrast, very few examples of transition metal oxides involving a mixed valence and a tetrahedral coordination of the transition element simultaneously, are actually known. In this respect, the oxide $YBaCo_4O_7$[1] and the magnetite Fe_3O_4[2,3] are of great interest, because they both exhibit the mixed-valence Co(II)/Co(III) and Fe(II)/Fe(III) and closely related structures isotypic to $LnBaZn_3AlO_7$[4] and spinel, respectively. Both "Co_4O_7" and "Fe_3O_4" frameworks consist of an ordered 1:1 stacking of two sorts of layers of polyhedra, with the triangular and kagomé configuration. The triangular layers, built up of CoO_4 or FeO_4 tetrahedra are similar in the two structures, whereas the kagomé layers differ by the nature of their polyhedra, i.e., consist of CoO_4 tetrahedra and FeO_6 octahedra for $YBaCo_4O_7$ and Fe_3O_4, respectively. In these two series of oxides, the magnetic properties are strongly coupled with structural transitions versus temperature, but are very different. The oxides $LnBa(Co,M)_4O_7$ [5−12] show magnetic properties reflecting a more or less frustrated magnetic structure, whereas Fe_3O_4[2,3] is ferrimagnetic with complex charge ordering.

The different behavior of iron oxides compared to copper, manganese, and cobalt oxides makes that the research of mixed valent iron oxides is really a challenge for understanding the magnetic and transport properties of strongly correlated systems. Exploring the possibility to generate new mixed valent Fe(II)−Fe(III) oxides we have synthesized a new series of ferrites, $Ca_{1-x}Y_xBaFe_4O_7$, which exhibits the trigonal structure of $YBaCo_4O_7$ at room temperature, but differently is shown to be ferrimagnetic with a T_C up to 270 K.

The compounds $Ca_{1-x}Y_xBaFe_4O_7$ were prepared in two steps: first a mixture of CaO, Y_2O_3, $BaCO_3$, and Fe_2O_3 in the molar ratio $6-6x:3x:6:10-x$ was heated in air at 900 °C for decarbonation; in a second step, the adequate amount of metallic iron was added in order to satisfy the formula $Ca_{1-x}Y_xBaFe_4O_7$.

The samples packed in bars were reacted in sealed tubes under primary vacuum at 1000 °C, in order to fix the oxygen content to "O_7".

The X-ray powder diffraction patterns of the above compounds were registered with a Panalytical X'Pert Pro diffractometer using Cu Kα radiation, combined with the TEM observations carried out with a FEI TECNAI G30 microscope. At room temperature, all X-ray diffraction patterns can be indexed in a trigonal cell: $a = 6.348(1)$ Å; $c = 10.370(2)$ Å for $CaBaFe_4O_7$ and $a = 6.318(1)$ Å; $c = 10.376(2)$ Å for $Ca_{0.2}Y_{0.8}BaFe_4O_7$ with the space group $P31c$, similarly to the space group used in the high temperature form of $YBaCo_4O_7$. This agrees with the electron diffraction study that evidences one single *hkl* condition: *hhl* $l = 2n$. The energy dispersive spectroscopy (EDS) confirms that their cationic contents "$Ca_{1-x}Y_xBaFe_4$" are very close to the nominal ones.

The structure refinements, carried out in the space group $P31c$ for the $CaBaFe_4O_7$ oxide, lead to a structure similar to that of $YBaCo_4O_7$, i.e., consists of an AB close packing of oxygen atoms, whose tetrahedral cavities are occupied by iron, forming two sorts of tetrahedral layers, triangular and kagomé layers stacked along $\vec{c}$ alternately (Figure 1), whereas cavities are occupied in an ordered way by calcium and barium. Thus, these results demonstrate the possibility to synthesize mixed valent Fe(II)−Fe(III) oxides, isotypic to the cobaltites of the series $LnBaCo_4O_7$.

The field-cooled (FC) magnetization curve registered with a SQUID magnetometer (MPMS Quantum Design) under 0.3T (Figure 2) shows a sharp increase of the magnetization around 270 K, indicating that the system orders magnetically and attains a large magnetization value contrasting with the low magnetization observed in isostructural $YBaCo_4O_7$.[9]

This strongly suggests a ferro- or ferrimagnetic background state. The zero-field-cooled (ZFC) magnetization curve (Figure 2) shows a broad maximum at around 150 K, i.e., much below T_C (270 K). At lower temperature below 120 K, the magnetization decreases rapidly, showing a strong irreversibility between the ZFC and FC data. Such a behavior might be explained if the value of the magnetic field (0.3 T) is smaller than the coercive field. The strong magnetic

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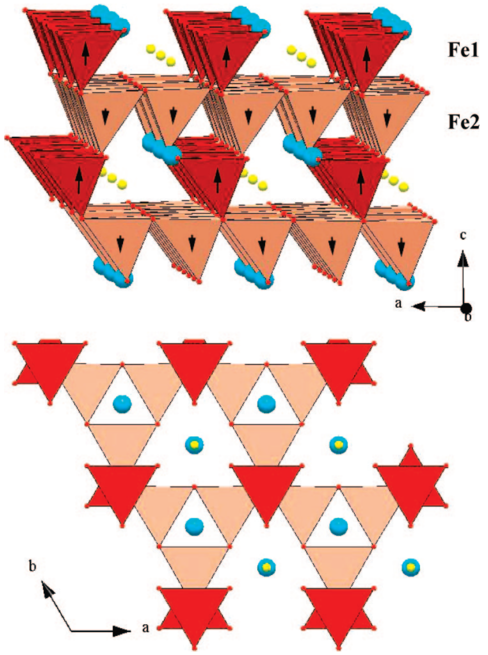

Figure 1. Perspective view of the $CaBaFe_4O_7$ structure (a) and projection along $\vec{c}$ (b) showing the two kinds of layers: kagomé layers (clear FeO_4 tetrahedra) and triangular layers (dark FeO_4 tetrahedra). Ba^{2+} and Ca^{2+} are represented by large and small spheres respectively. The arrows indicate the possible spin coupling of the Fe^{2+}/Fe^{3+} species.

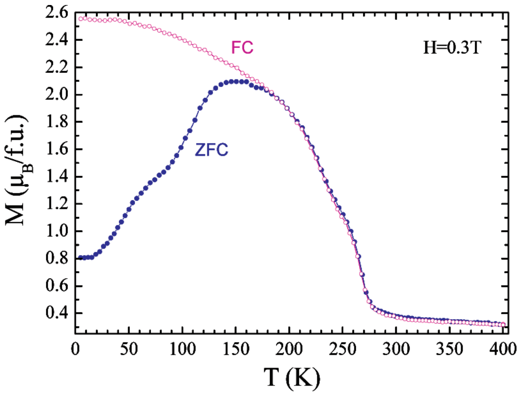

Figure 2. Magnetization M(T) curve of $CaBaFe_4O_7$: zero field cooled (ZFC) in solid symbol and field cooled (FC) in open symbol.

irreversibility is confirmed by the isothermal field driven magnetization $M(H)$ curves collected at four different temperatures (Figure 3).

A large hysteresis loop is observed at 5 K (Figure 3a) with a remanent magnetization (M_R) value of ~2.0 μ_B and a coercive field (H_C) of ~0.74 T larger than the magnetic field used for the ZFC-FC measurements. These high values of M_R and H_C at low temperature show that $CaBaFe_4O_7$ behaves as a hard ferri- or ferromagnet. The particular shape of the loop at 5K, involving a step like behavior at 0.4 T can be explained by a strong pinning of the domain walls. As the temperature increases, H_C decreases progressively (Figure 3a−c) and finally above T_C, a linear behavior of M(H), corresponding to a paramagnetic state is observed (not shown).

The curves collected below T_C show a lack of magnetization saturation even for magnetic field of 5 T. This lack of saturation together with the large M_R and H_C values strongly

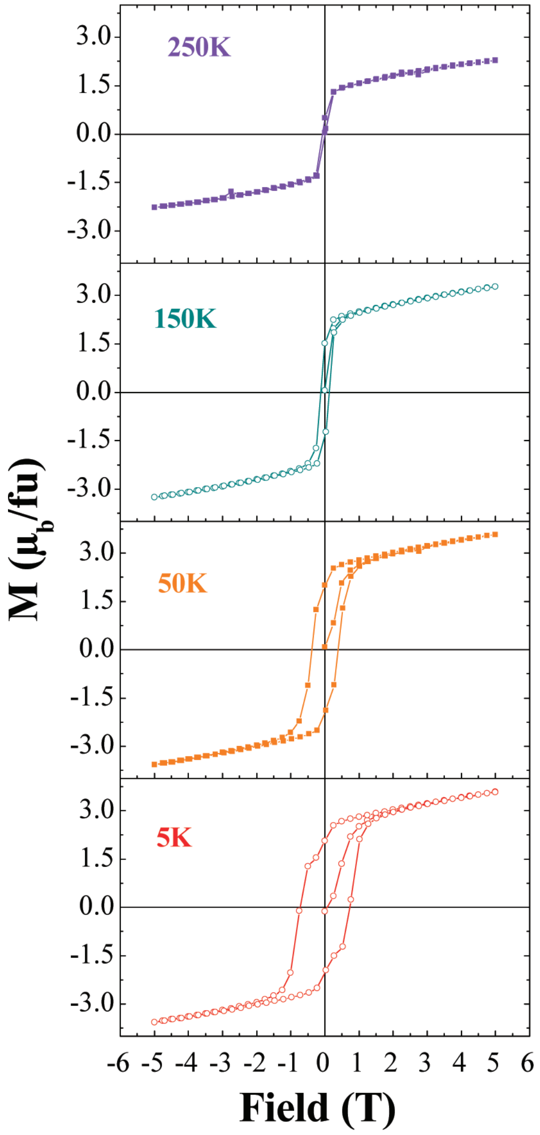

Figure 3. Magnetic field dependence of the magnetization, $M(H)$ for $CaBaFe_4O_7$ at four different temperatures: (from bottom to top) (a) 5, (b) 50, (c) 150, and (d) 250 K.

support the existence of a ferrimagnetic state for $CaBaFe_4O_7$. This is especially true if one considers the highest value of the magnetization, 3.5 μ_B/f.u., that is reached for this compound. Bearing in mind that in this phase, both Fe(II) and Fe(III) spins are located in tetrahedral sites, and consequently are both in high spin (HS) configuration, i.e., $e_g{}^3t_{2g}{}^3$ for Fe(II) and $e_g{}^2t_{2g}{}^3$ for Fe(III), a ferromagnetic alignment of all iron spins would lead to a too much higher value of the resulting magnetic moment (~18 μ_B/f.u.). In fact, the analysis of the structure shows that there exist two sites for iron cations: 75% are located in kagomé layers (Fe2 site) and 25% sit in the triangular layers (Fe1 site). Consequently it is most probable that these oxides are ferrimagnetic, the iron cations showing a ferromagnetic component in each sublattice (kagomé and triangular). Then, considering an antiferromagnetic coupling between the two sublattices, the ferrimagnetism could result from the non compensation of the sublattice magnetizations (Figure 1a). Moreover, the geometric frustration (Figure 1b) and the possible charge ordering of Fe^{2+} and Fe^{3+} point toward a complex magnetic structure as reported for the charge ordered ferrimagnetic compounds RFe_2O_4.[13] In that respect, a neutron diffraction study should be performed to solve the magnetic structure of $CaBaFe_4O_7$. The ρ(T) curves registered under 0 and 7 T (not shown here) show that this oxide exhibits a semiconducting behavior in the whole temperature range, and no magnetoresistance is detected.

Bearing in mind the crucial role of iron valence in the magnetic properties of such oxides, the substitution of yttrium for calcium was studied. The solid solution $Ca_{1-x}Y_xBaFe_4O_7$, synthesized for $0 \leq x \leq 0.8$, shows a continuous decrease of its cell parameters, as x increases. Remarkably, the different compounds of the whole series remain ferrimagnetic, T_C and M_R decreasing and H_C increasing as x increases, as illustrated from the magnetic data of the limit compound $Ca_{0.2}Y_{0.8}BaFe_4O_7$ (Figure 4). The ZFC and FC magnetization curves of this phase (inset Figure 4a) show indeed that T_C has decreased to ~160 K, whereas there exists a larger irreversibility between the ZFC and FC data than in $CaBaFe_4O_7$. The M(H) hysteresis loop at 5 K (Figure 4) shows that the coercive field has increased up to $H_C \approx 1.26$ T. The decrease of the remanent magnetization, down to $M_R \approx 1.3\ \mu_B$/f.u., and the highest value of magnetization, which reaches only 2.5 μ_B/f.u., is compatible with the decrease in magnetic moment per iron because of the increase in Fe^{2+} content with x.

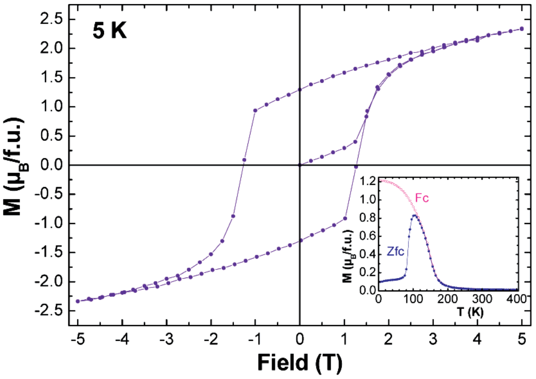

Figure 4. Magnetic field dependence of the magnetization, M(H) for $Ca_{0.2}Y_{0.8}BaFe_4O_7$ at 5K. Inset: ZFC and FC M(T) curves (0.3T).

In conclusion, a new series of iron oxides, with the generic formula $Ca_{1-x}Y_xBaFe_4O_7$ has been synthesized, which is characterized by the mixed valence Fe(II)−Fe(III), with iron in tetrahedral coordination. Though they are isotypic to the $LnBaCo_4O_7$ oxides, these new ferrites exhibit very different magnetic properties, and can be described as ferrimagnetic with a T_C up to 270 K. In this respect they are more closely related to the magnetite Fe_3O_4. Studies are in progress on lanthanide series $Ca_{1-x}Ln_xBaFe_4O_7$ in order to understand the influence of the Ln^{3+} size upon those properties. The close structural relationships of these oxides with the spinel structure of magnetite, opens the route to numerous investigations in order to understand the magnetism of these compounds and to generate new ferro/ferrimagnets.

Supporting Information Available: X-ray powder patterns of $Ca_{1-x}Y_xBaFe_4O_7$ for $x = 0, 0.2, 0.8$; magnetization M(T) curves of $Ca_{1-x}Y_xBaFe_4O_7$ for $x = 0.2, 0.5$; experimental [001], $[1\bar{1}0]$, and [100] zone axis ED diffraction patterns of $CaBaFe_4O_7$; and atomic coordinates of $CaBaFe_4O_7$ (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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