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Gigantic effect of iron doping upon magnetism in the «114» magnetoelectric $CaBaCo_4O_7$

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The investigation of the $CaBaCo_{4-x}Fe_x0_7$ oxide shows that a huge decrease of ferrimagnetism is produced for very low Fe contents ($x < 0.05$) at the benefit of magnetic phase separation and magnetic frustration. This gigantic effect of iron doping at the Co^{3+} sites in $CaBaCo_4O_7$ is compared to that produced by diamagnetic Ga^{3+} and Al^{3+} dopants, showing that the antiferromagnetic interactions between the dopant Fe^{3+} and the Co^{2+} ferromagnetic chains has a crucial role in the destabilization of the ferrimagnetic structure, whereas the triangular geometry of the cobalt sublattice imposes the appearance of magnetic frustration.

1. Introduction

Transition metal oxides involving a triangular geometry of their metallic sub-lattice have attracted significant interest due to their ability to generate magnetic frustration which can compete with magnetic ordering, leading to various geometrically frustrated magnets [1–10].

Besides the spinel and pyrochlore families a new class of frustrated magnets has been obtained with the discovery of the hexagonal "114" $LnBaCo_4O_7$ cobaltites [11–13] that were shown to exhibit complex magnetic properties [14–16]. The oxide $CaBaCo_4O_7$, which belongs to this structural family has a unique behavior, due to the fact that its geometric frustration can be partially lifted due to a large orthorhombic distortion of the hexagonal symmetry, leading to charge ordering and ferrimagnetism below 60 K [17,18]. Moreover, this non centrosymmetric oxide was shown to exhibit gigantic electric polarization and strong magnetoelectric coupling [19,20]. Recently, its investigation from *ab initio* calculations showed that it is a pyroelectric [21].

The particular behavior of $CaBaCo_4O_7$ is mainly dictated by the non collinear arrangement of the cobalt spins which form ferromagnetic Co^{2+} zig-zag chains running along the *b* direction. The antiferromagnetic (AFM) coupling of those Co^{2+} chains with isolated Co^{3+} species of other sites suggests that it should be possible to modify the magnetism of this oxide in a selective way by an ordered substitution either at the Co^{2+} or at the Co^{3+} sites respectively. The substitution of cobalt by diamagnetic cations supports this viewpoint. It was indeed shown that the doping of zinc at the Co^{2+} sites with less than 3% Zn switches the ground state abruptly from ferrimagnetic to antiferromagnetic, induces magnetic frustration around the doped centers, together with an evolution toward incommensurate magnetic phases and spin-flop transition [22,23]. In contrast, the effect of substitution at the Co^{3+} sites by gallium or aluminum is much less dramatic, especially for low dopant contents, where the ferrimagnetic ground state is only gradually decreased [24,25].

In the present work, we focus on the doping of $CaBaCo_4O_7$ with trivalent iron and we compare the effect with that produced by trivalent diamagnetic cations (Ga, Al). We show that tiny amounts of Fe^{3+}, i.e. less than 1.5%, practically suppresses the ferrimagnetic state, resulting in a complex phase separated magnetic ground state.

2. Experimental

The samples $CaBaCo_{4-x}Fe_xO_7$ with x ranging between 0 and 0.05 were synthesized from the respective mixtures of $CaCO_3$ (99.8%), $BaCO_3$ (99.8%), Co_3O_4 (99.7%) and Fe_2O_3 (99.9%) all from Alfa Aesar.

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The oxygen stoichiometry of the cobalt oxide was found to be $CoO_{1.28}$ instead of $CoO_{1.33}$. The appropriate proportions of the starting materials were weighed and mixed thoroughly using a mortar pestle, adding ethanol for homogeneous mixing. The mixtures were first heated overnight in air at 1173 K. The mixtures were then ground and pressed in the form of parallelepipedic bars and heated in air for 24 h at 1373 K. All the samples finally were quenched to room temperature in order to stabilize the "114" phase.

The X-ray diffraction patterns were registered with a Panalytical X'Pert Pro diffractometer under a continuous scanning mode in the 2θ range $10°-120°$ and step size $\Delta 2\theta = 0.017°$ with Cu Kα radiation. The energy dispersive spectroscopy (EDS) analysis carried out with an analyzer (LINK) mounted on a scanning electron microscope (Oxford Instruments) allowed the contents of the major elements (Ca, Ba, Co) to be determined, confirming the nominal composition in the limit of the accuracy (±2%). The iodometric titration of these samples confirms that the oxygen stoichiometry fixed to "O_7" within the limit of accuracy of ±0.02. The d. c. magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer with a variable temperature cryostat (Quantum Design, San Diego, USA). All the d. c. measurements were carried out in an applied field of 0.3 T. The a. c. susceptibility, $\chi_{ac}(T)$ was measured with a PPMS (Quantum Design, San Diego, USA) with the frequency ranging from 10 Hz to 10 kHz. In all the a.c. measurements H_{ac} and H_{dc} field were kept fixed at 10 Oe and 0 Oe, respectively. All the magnetic properties were registered on dense ceramic bars of dimensions ~$4 \times 2 \times 2$ mm^3.

3. Results and discussion

For the conditions of synthesis described above, the powder X-ray diffraction (PXRD) patterns of the $CaBaCo_{4-x}Fe_xO_7$ oxides with $0 < x < 0.05$ attest of the purity of the samples (see Fig. 1(a) for $x = 0.05$). Rietveld refinements using FULPROF program [26] confirm the orthorhombic $Pbn2_1$ symmetry of this phase, with cell parameters (Table 1) closely related to those of the hexagonal oxides, $a_O \simeq a_H$, $b_O \simeq a_H\sqrt{3}$, $c_O \sim c_H$. Note that though all the compositions remain orthorhombic within the doping range, the orthorhombic distortion with respect to the hexagonal structure, $D = \frac{b}{\sqrt{3}} - a/a$ [18], decreases as the dopant concentration increases (Fig. 1(b)).

The dc magnetization versus temperature, registered under an applied field of 0.3 T (Fig. 2) shows that not only T_C decreases as the doping concentration increases, but the magnetization decreases abruptly from 0.67 μ_B/f.u. for $x = 0$ (Fig. 2(a)) to 0.01 μ_B/f.u. for $x = 0.05$ (Fig. 2(e)) at 5 K. This signifies a spectacular drop of the initial ferrimagnetic ground state by Fe doping. The derivative (dM/dT) plots as a function of temperature (Fig. 2(f)–(j)) shows that this evolution is still more complex. One indeed observes a broadening of the derivative curves as x increases to 02–0.03 (Fig. 2(g) and (h)), leading finally to a clear splitting of the curves for $x = 0.04–0.05$ (Fig. 2(i) and (j)). This suggests the formation of a phase separated system, where the initial ferrimagnetic phase coexists with a new magnetic phase. This feature shows some similarity with the behavior of the Zn-doped $CaBaCo_4O_7$, for which both a decrease of T_C for the ferrimagnetic phase, and the appearance of an incommensurate magnetic phase were observed by neutron diffraction [23]. However, here the disappearance of the ferrimagnetic phase is much more drastic and the nature of the new magnetic phase is most probably different. Moreover, another new magnetic transition appears at ~88 K for $x = 0.05$ (Fig. 2(j)), which is more clearly detected from a kink in the range 85 K (for $x = 0.02$) to 88 K (for $x = 0.05$) in the $M^{-1}(T)$ data (Fig. 3) for other doped compositions.

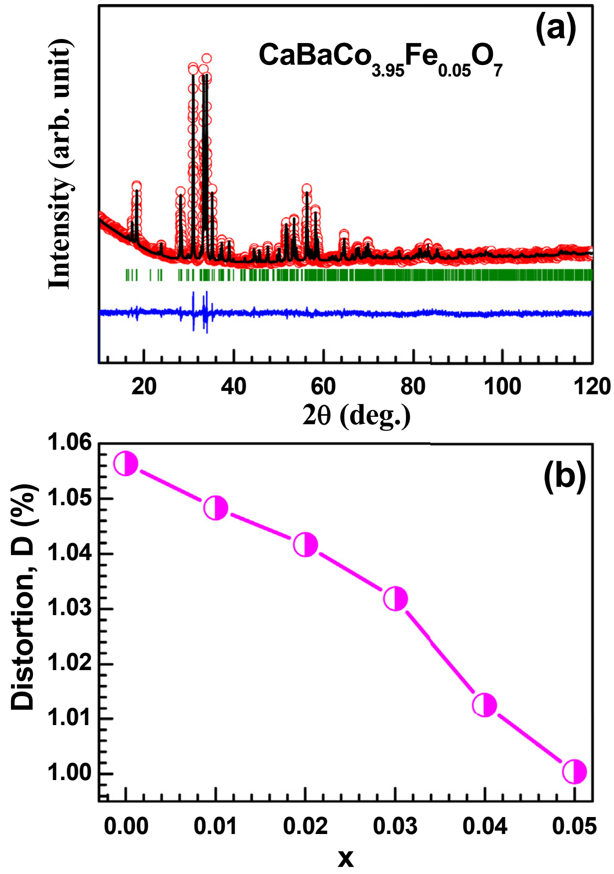

Fig. 1. (a) X-ray diffraction patterns (red circles) along with the fits (black lines) of $CaBaCo_{3.95}Fe_{0.05}O_7$. The residues are shown as blue lines at the bottom and the Bragg peaks are shown as green bars. (b) The variation of the distortion $D = \frac{\frac{b}{\sqrt{3}} - a}{a}$ with x. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Lattice parameters for $CaBaCo_{4-x}Fe_xO_7$ ($0 \le x \le 0.05$) refined with space group P*bn2*$_1$.

Composition	a(Å)	b (Å)	c (Å)	V (Å^3)
$CaBaCo_4O_7$	6.287(1)	11.004(6)	10.192(8)	705.161(7)
$CaBaCo_{3.99}Fe_{0.01}O_7$	6.287(6)	11.004(4)	10.191(5)	705.183(5)
$CaBaCo_{3.98}Fe_{0.02}O_7$	6.288(2)	11.004(5)	10.191(4)	705.223(3)
$CaBaCo_{3.97}Fe_{0.03}O_7$	6.288(4)	11.004(2)	10.191(6)	705.256(8)
$CaBaCo_{3.96}Fe_{0.04}O_7$	6.288(9)	11.003(1)	10.192(3)	705.273(3)
$CaBaCo_{3.95}Fe_{0.05}O_7$	6.289(4)	11.002(6)	10.192(4)	705.322(2)

The isothermal magnetization curves registered at 5 K (Fig. 4) reflect the strong effect of Fe-doping upon the magnetic ground state of these compounds. The square shape of the M(H) curve is retained up to $x = 0.02$ (Fig. 4(b)) and is significantly distorted by increasing the doping level to $x = 0.03–0.04$ (Fig. 4(c) and (d)). For $x = 0.05$ (Fig. 4(e)) a splitting of the hysteresis loop into two loops is observed, similar to that previously described in several antiferromagnetic oxides and which was attributed to a metamagnetic transition [27,28]. Bearing in mind the shape evolution of the M(T) derivative curves (Fig. 2(f)–(j)) centered around 50 K, we have measured isothermal magnetization around this temperature (Fig. 5). One can notice the change in shape of the M(H) curves for $x = 0.02$ measured at 40 and 50 K (Fig. 5(b)). The curve at 40 K has a regular shape, like the parent phase, with a smaller coercive field at higher temperature, as expected. But for the curve at 50 K besides