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The “114” Cobaltites and Ferrites :
New Routes to Ferrimagnetism and Magnetic Frustration

Dedicated to Professor Martin Jansen in the honour of his 65th Birthday

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Abstract

An overview of the magnetic properties of the “114” cobaltites and ferrites in connection with their crystal structure, built up of triangular and kagomé layers of CoO₄ tetrahedra is presented. These oxides can be classified into three different structural types according to their room temperature structure: the trigonal P31c phases LnBaCo₄O₇ and CaBaFe₄O₇, the orthorhombic Pbn2₁ CaBaCo₄O₇ phase and the cubic LnBaFe₄O₇ oxides. The magnetic properties show complex transitions for LnBaCo₄O₇ oxides, whereas spin glass like behavior is observed for LnBaFe₄O₇ and ferrimagnetic like properties are observed for CaBaFe₄O₇ and CaBaCo₄O₇. The topotactic oxidation of those oxides is also discussed.

Transition metal oxides with a triangular geometry of their oxygen framework have been the object of numerous investigations these last few decades, due to their ability to exhibit magnetic frustration [1-2]. In this respect, the family of “114” cobaltites – $\text{LnBaCo}_4\text{O}_7$ ($\text{Ln}=\text{lanthanide and Y}$) [3-4] $\text{CaBaCo}_4\text{O}_7$ [5] – and of “114” ferrites - $\text{LnBaFe}_4\text{O}_7$ [6] and $\text{CaBaFe}_4\text{O}_7$ [7] – are of great interest. In these compounds, the transition element shows the mixed valence, $\text{Co}^{2+}/\text{Co}^{3+}$ or $\text{Fe}^{2+}/\text{Fe}^{3+}$ and exhibits the tetrahedral coordination exclusively, leading to exotic magnetic and electron transport properties. In the present paper, we give an overview of the magnetic and transport properties of these oxides, in connection with their close structural relationships.

The $\text{LnBaCo}_4\text{O}_7$ series : complex magnetic and electronic transitions and magnetic frustration.

Discovered by Mueller-Buschbaum for the oxide $\text{LnBaZn}_3\text{AlO}_7$ [8], the “114” hexagonal structure, has been then reported for a series of cobaltites $\text{LnBaCo}_4\text{O}_7$ with $\text{Ln}=\text{Tb, Dy, Ho, Er, Tm, Yb, Ln and Y}$ [3-4, 9-12]. In fact, there is still an ambiguity about the space group which can be either hexagonal $P6_3mc$ as shown for $\text{HoBaCo}_4\text{O}_7$ [13] or $P31c$ as observed for $\text{YbBaCo}_4\text{O}_7$ [14], but the latter does not affect significantly the description of the structure. Thus, the oxygen framework of these oxides can be described as an “ABCB” (chch) stacking of close packed “ O_4 ” and “ BaO_3 ” layers alternately (Fig. 1a-b) whose tetrahedral cavities are occupied by cobalt cations. In other words, this structure can be described as a pure tetrahedral framework, where the CoO_4 tetrahedra form two sorts of layers (Fig. 1c-d), triangular (T) and kagomé (K) layers stacked along c alternately, whereas the Ln^{3+} cations sit in the octahedral cavities.

The magnetic studies of Y-114 [3,11] show that this oxide may be antiferromagnetically ordered at low temperature, suggesting a spin glass behavior with $T_c \sim 66$ K or a weak ferromagnetic coupling rather than ferrimagnetism at low temperature, as illustrated from the $M(T)$ curve registered under 50mT (Fig. 2). Importantly, the neutron diffraction study of this oxide [15] shows that it undergoes a structural transition from hexagonal ($P31c$) to orthorhombic “ $a \times a\sqrt{3} \times c$ ” ($Pbn2_1$), below $T_S = 313$ K, and correlatively short range diffuse magnetic scattering appears below this temperature, giving rise finally to 3 D long-range antiferromagnetic ordering below $T_N = 110$ K. In other words, the geometric frustration in YBaCo_4O_7 is relieved below 313 K, thanks to a first order structural transition. The high sensitivity of the magnetic frustration to the structural distortion has encouraged

numerous studies about the effect of substitution of cobalt and Y by various cations [16-23], upon the magnetic and transport properties of this oxide. All these investigations cannot be detailed here. However, it is worth pointing out that correlatively the magnetic susceptibility, the resistivity (ρ) and the thermoelectric power (S) show a sharp increase at T_S , as the temperature decreases and moreover T_S decreases dramatically as the size of the Ln^{3+} site cation decreases as illustrated by the $S(T)$ curves of $\text{Y}_{1-x}\text{Yb}_x\text{Co}_4\text{O}_7$ (Fig. 3), which show that T_C decreases from 313 K for $x=0$ to 165 K for $x=1$. In the same way, the low substitution level of divalent (Zn^{2+}) or trivalent cation (Al^{3+} , Ga^{3+}) for cobalt has a strong impact upon this structural/electrical transition, as illustrated from the thermoelectric power curves $S(T)$ (Fig. 4) which show that small levels of trivalent cations, such as Al, suppress the transition, whereas small levels of divalent cations, such as Zn, decrease the transition temperature T_S .

CaBaCo₄O₇: ferrimagnetic like properties

Recently synthesized in air, like the oxides $\text{LnBaCo}_4\text{O}_7$, the cobaltite $\text{CaBaCo}_4\text{O}_7$ [5] does not exhibit at room temperature the hexagonal symmetry, but the orthorhombic symmetry, compatible with the $\text{Pbn}2_1$ space group of the low temperature form of $\text{LnBaCo}_4\text{O}_7$ series. Importantly the orthorhombic cell ($a=6.288\text{\AA}$, $b=11.007\text{\AA}$, $c=10.194\text{\AA}$) shows the largest distortion that has ever been observed with respect to the hexagonal $\text{P}31\text{c}$ structure. Thus, in contrast to the $\text{LnBaCo}_4\text{O}_7$ oxides, no structural transition is observed for $\text{CaBaCo}_4\text{O}_7$ in the whole temperature range from 4K to 300K.

The $\text{CaBaCo}_4\text{O}_7$ structure (Fig. 5) is closely correlated to that of the hexagonal $\text{LnBaCo}_4\text{O}_7$ oxides (Fig. 1). It consists of ordered 1:1 stacking of $[\text{BaO}_3]_\infty$ and $[\text{O}_4]_\infty$ close packed layers, whose tetrahedral cavities are occupied by cobalt cations, whereas Ca^{2+} cations sit in the octahedral cavities. Thus, like for $\text{LnBaCo}_4\text{O}_7$ oxides, the structure of $\text{CaBaCo}_4\text{O}_7$ can be described as the 1:1 stacking of kagomé and triangular layers of CoO_4 tetrahedra. However this structure differs from the other “114” cobaltites – hexagonal and orthorhombic – by a very strong buckling of the CoO_4 tetrahedra of the kagomé layers (Fig. 5).

The magnetic properties of this phase are remarkably different from that observed for the $\text{LnBaCo}_4\text{O}_7$ series, in spite of its very close structural relationships. The field cooled (FC) magnetization curve (Fig. 6) shows a sharp increase of the magnetization at $T_C=70\text{K}$, suggesting a ferro-or ferrimagnetic ground state. This unique transition is also observed from the ac-susceptibility curve vs temperature (Fig. 7), confirming the existence of a ferromagnetic component with $T_C=70\text{K}$. Nevertheless the maximum magnetization value of

0.65 μ_B /fu., far below the theoretical value for ferromagnetic cobalt, indicates that this compound is ferrimagnetic, in agreement with the fact that two sorts of sites are available for cobalt, and is possibly frustrated due to the particular geometry of the kagomé lattice.

Another interesting characteristic of this phase deals with its magnetic hysteresis loop at 5K (Fig. 8), which exhibits a large coercive magnetic field of 2T. Note that H_c decreases rapidly as T increases, down to 0.5T at 30K. The strong irreversibility between the zero field cooled (ZFC) and field cooled (FC) curves observed on $\chi(T)$ (Fig.6) can then be explained by the low value of the applied magnetic field (0.3T) compared to the much larger H_c value (2T).

This remarkable difference in the magnetism of $\text{CaBaCo}_4\text{O}_7$, compared to $\text{LnBaCo}_4\text{O}_7$ series, in spite of their structural similarities, can be explained by two factors : (i) the $\text{Co}^{2+}:\text{Co}^{3+}$ ratio which is of 1 in the Ca phase against 3 in the Ln oxides (ii) the geometric frustration which remains maximum (close to the hexagonal symmetry) in the Ln phases, and is relieved by the buckling of the kagomé layers in the Ca phase. Nevertheless, considering the electronic structures of Co(II), i.e. $e_g^4 t_{2g}^3$ and Co(III), i.e. $e_g^3 t_{2g}^3$ for high spin or $e_g^4 t_{2g}^2$ for low spin, it appears that the theoretical magnetic moment for a ferromagnetic alignment of the spins – 10 μ_B to 14 μ_B – is much higher than the experimental value (0.6 μ_B). Thus, ferrimagnetism should be considered, due to the antiferromagnetic coupling of the two cobalt sublattices Co 1 triangular layers (25%) and Co 2 kagomé layers (75%). Nevertheless such a hypothesis is still not sufficient to explain the low value of the magnetic moment, suggesting that the magnetic structure is complex and might be partly influenced by the geometric frustration inherent to the structure. Further investigation of the magnetic structure of this phase, using neutron diffraction will be needed to understand its behavior.

The $\text{Ca}_{1-x}\text{Y}_x\text{BaFe}_4\text{O}_7$ series: Ferrimagnetism up to 270K

Exploring the possibility to generate new mixed valent Fe(II)-Fe(III) ferrites, a new series of “114” ferrites, $\text{Ca}_{1-x}\text{Y}_x\text{BaFe}_4\text{O}_7$ was recently discovered [6], for $0 \leq x \leq 0.80$.

These oxides, isotypic to YBaCo_4O_7 , exhibit the same hexagonal symmetry, with the same P31c space group as the room temperature form of the cobalt phases $\text{LnBaCo}_4\text{O}_7$. The stabilization of such a structure, where all iron cations exhibit the tetrahedral coordination, is quite remarkable, bearing in mind that such a coordination is rarely observed for Fe^{2+} in oxides. Moreover, no transition to an orthorhombic form is observed as the temperature is decreased from 300K to 4.2K, in contrast to cobalt oxides. The comparison of the trigonal P31c structure of $\text{CaBaFe}_4\text{O}_7$ (Fig. 1) and the orthorhombic Pbn2₁ structure of $\text{CaBaCo}_4\text{O}_7$

(Fig.5) illustrates this difference between iron and cobalt oxides. In other words, iron favours the triangular geometry in the whole temperature range, whereas cobalt induces the buckling of the tetrahedra.

The study of the magnetization versus temperature (Fig. 9) shows that, surprisingly, $\text{CaBaFe}_4\text{O}_7$ exhibits a sharp increase of the magnetization around 270K and attains a magnetization value, much larger than that obtained for YBaCo_4O_7 and even than for $\text{CaBaCo}_4\text{O}_7$ (Fig.6).

Thus, $\text{CaBaFe}_4\text{O}_7$ exhibits a ferro-or ferrimagnetic ground state. The zero field cooled (ZFC) $M(T)$ curve, which goes through a maximum around 150K, shows a strong irreversibility between FC and ZFC data, due to the fact that this oxide exhibits a large coercive field, i.e. larger than the applied magnetic field (0.3T). Indeed, the $M(H)$ curve registered at 5K (Fig.10) shows that this oxide is a hard ferri-or ferromagnet with a coercive field $H_c \sim 0.74\text{T}$ and a remanent magnetization $M_R \sim 2.0\mu_B$. The particular shape of the loop at 5K, showing a step like behavior at 0.4T, is explained by a strong pinning of the domain walls. The lack of magnetization saturation of the $M(H)$ curves even for a magnetic field of 5T, together with the large M_R and H_c values indicate that $\text{CaBaFe}_4\text{O}_7$ is a ferrimagnet. This view point is supported by the magnetization which reaches only a maximum value of $3.5 \mu_B / \text{f.u.}$ Considering that both ions Fe(II) and Fe(III) sit in tetrahedral sites and are consequently in high spin configuration, i.e. $e_g^3 t_{2g}^3$ for Fe(II) and $e_g^2 t_{2g}^3$ for Fe(III), a much higher value of the magnetic moment ($\sim 18 \mu_B / \text{f.u.}$) would be expected for a ferromagnetic alignment of all the iron spins. Bearing in mind the existence of two sites for iron, similarly to cobalt in $\text{CaBaCo}_4\text{O}_7$, suggests strongly that $\text{CaBaFe}_4\text{O}_7$ is ferrimagnetic with $T_c \sim 270\text{K}$, due to antiferromagnetic coupling between the triangular Fe1 sites and the kagomé Fe2 sites. However, this ferrimagnetism is not sufficient to explain the rather low value of the experimental magnetic moment ($3.5 \mu_B / \text{f.u.}$), so that geometric frustration and possible charge ordering may play a role in such a magnetic structure which should be investigated in the future by neutron diffraction. The substitution of yttrium for calcium in this phase, shows that the P31c trigonal structure is maintained for the series $\text{Ca}_{1-x}\text{Y}_x\text{BaFe}_4\text{O}_7$, in the whole composition range, $0 \leq x \leq 0.80$, the cell parameters decreasing as x increases. Remarkably the compounds of this series remain ferrimagnetic, T_c decreasing down to 160 K as x increases. Similarly M_R decreases, and H_c increases as x increases. The physics of these compounds should be further investigated in the future in order to understand the effect of the size of A cations and valency of iron upon the magnetic properties of these materials.

YBaFe₄O₇: a spin glass like oxide with a new cubic structure closely related to those of CaBaFe₄O₇ and cobaltites.

Differently from YBaCo₄O₇, the ferrite YBaFe₄O₇ exhibits a face centred cubic cell, with a $\sim 8.96\text{\AA}$. In fact, its cubic structure (Fig.11) is closely related to that of YBaCo₄O₇ (Fig.1). It consists of similar kagomé (K) and triangular (T) layers of FeO₄ tetrahedra parallel to (111)_C, stacked along $\langle 111 \rangle_C$ in such a way that one kagomé layer alternates with one triangular layer (Fig.11a). The geometry of the kagomé and triangular layers is identical in the two structures forming large triangular windows but the relative positions of the triangular layers in the YBaFe₄O₇ structure (Fig.11b) is different from that in YBaCo₄O₇ (Fig.1d) : in the cubic YBaFe₄O₇ the FeO₄ tetrahedra of one triangular layer out of two is shifted by $a/2$ in the (111) plane with respect to the YBaCo₄O₇ structure. It results that the triangular tunnels running along $\langle 110 \rangle_C$ in YBaFe₄O₇ are perfectly regular (Fig.11b), whereas the corresponding $\langle 100 \rangle_H$ tunnels in YBaCo₄O₇ are distorted (Fig.1d). Thus, the cubic [Fe₄O₇]_∞ framework of YBaFe₄O₇ is deduced from the hexagonal [Co₄O₇]_∞ framework of YBaCo₄O₇ by shifting the Co(Fe) tetrahedra in one triangular layer out of two, generating new kagomé layers oriented at 70° from the original (001)_H kagomé layers. As a consequence, the oxygen framework of YBaFe₄O₇ consists also of a stacking of close packed “O₄” and “BaO₃” layers alternately, but the stacking 1:1 sequence is cubic “ABC” (ccc) (Fig.11c) instead of hexagonal ABCB (hchc) for YBaCo₄O₇ (fig.1b). The close packing of YBaFe₄O₇ can be derived from the close packing of the spinel structure. This can be done by replacing one oxygen atom out of four by barium in half of the “O₄” layers of the “O₈” spinel framework. In this respect, one would expect for such a phase, ferromagnetic properties similar to the spinel or to the hexagonal ferrites which also contain similar close packed “BaO₃” layers associated to “O₄” hexagonal layers. However, the distribution of the Fe²⁺/Fe³⁺ species in YBaFe₄O₇ is fundamentally different from that observed for spinels and for hexagonal ferrites, since iron is distributed in octahedral and tetrahedral sites in the latter systems, whereas it exhibits exclusively the tetrahedral coordination in YBaFe₄O₇. Remarkably, the iron cations in the YBaFe₄O₇ structure form a tetrahedral [Fe₄]_∞ framework identical to that observed in pyrochlores, suggesting that such an arrangement may induce magnetic frustration, like it was observed in many oxides with the pyrochlore structure [1-2]. The $\chi(T)$ ZFC curve of YBaFe₄O₇ which shows a maximum at 45K with a cusp like shape and the FC curve which is quasi temperature independent below 45K (Fig. 12a) are strongly in favour of a spin glass like behavior. The ac-susceptibility measurements performed at two frequencies (Fig.12b) confirm the existence of a cusp-like feature peaking at T_g=45K and show a slight increase of T_g by

about 1K (inset Fig.12b) as f increases. These results definitely demonstrate that YBaFe_4O_7 is, in contrast to $\text{CaBaFe}_4\text{O}_7$ a spin glass like oxide.

Topotactic oxidation in the “114” family

Another unique property of this family of compounds deals with its ability to reversibly uptake oxygen at low temperature (100-350 °C) and release this surplus oxygen at upper temperature in the range of 350-500 °C. Such a phenomenon is of great interest in order to generate oxidized phases with an original structure and unique physical properties. Moreover such materials exhibit a great potential for application as cathode for ITSOFC [24].

This attractive property was first reported by Chmaissem et al [25] for YBaCo_4O_7 . These authors prepared the phase $\text{YBaCo}_4\text{O}_{8.1}$ by a controlled oxidation of the kagomé lattice compound YBaCo_4O_7 , leading to a new closely related structure, with the $\text{Pbc}2_1$ space group which corresponds to a doubled superstructure unit cell with respect to the orthorhombic $\text{Pbn}2_1$ low temperature form of YBaCo_4O_7 . This extra oxygen induces a considerable displacement of the original oxygen atoms, so that the coordination of cobalt is significantly modified, showing both, corner-sharing CoO_4 tetrahedra and edge-sharing CoO_6 octahedra, in the unique structure of $\text{YBaCo}_4\text{O}_{8.1}$.

The study of the oxygen storage capability of $\text{LnBaCo}_4\text{O}_7$ [26] showed that large amounts of oxygen up to 1.50 mole/f.u. can be “inserted” into the structure and released out of the matrix in a rather narrow temperature range between ~ 200 °C and 450 °C. Moreover these authors showed that the amount of “inserted” oxygen is highly dependent on the size of the lanthanide, i.e. increasing with the size of the latter from Lu to Dy, and on the experimental conditions of oxidation (Fig. 13). The recent study of $\text{YBaCo}_4\text{O}_{8.5}$ shows the extraordinary mobility of oxygen and its complex ordering [27]. Detailed studies of these oxidized compounds will be necessary to understand their various structures.

Recently, we have explored the oxidation of $\text{CaBaCo}_4\text{O}_7$ [28]. In contrast to YBaCo_4O_7 , the annealing of this compound in air , or in an oxygen flow up to 500 °C does not lead to a significant increase of the oxygen content, the “114” structure being destroyed above 475 °C. In order to avoid such a decomposition, attempts were made to oxidize $\text{CaBaCo}_4\text{O}_7$ by electrochemical technique at room temperature, using a platinum wire as counter electrode, and Hg/HgO as reference electrode. Sintered pellets of $\text{CaBaCo}_4\text{O}_7$ were used as positive electrode and 1M KOH solution was used as electrolyte. The voltametric polarization performed in the 0.2-0.6V potential window allowed $\text{CaBaCo}_4\text{O}_7$ to be oxidized into $\text{CaBaCo}_4\text{O}_{7.5}$. Remarkably, the oxidation of $\text{CaBaCo}_4\text{O}_7$ into $\text{CaBaCo}_4\text{O}_{7.5}$

reduces the orthorhombic distortion leading to the hexagonal symmetry, similar to that of YBaCo_4O_7 . A detailed structural investigation of this phase will be necessary to understand this phenomenon;

The investigation of the oxidation of iron compounds is still at its very beginning [28], but appears already very promising. The oxidation of the cubic ferrite YBaFe_4O_7 in an oxygen flow, appears in the same temperature range as for YBaCo_4O_7 , i.e. below 400 °C, leading to YBaFe_4O_8 . Curiously, the latter phase remains cubic with a large increase of the cell volume from 719.2 Å³ to 741.7 Å³. A structural study is in progress to understand this topotactic oxidation. The case of $\text{CaBaFe}_4\text{O}_7$ is different, though it can also uptake 1 oxygen per f.u. under an oxygen flow between 75 °C and 450 °C, leading to the oxide $\text{CaBaFe}_4\text{O}_8$. This phase shows in fact a broadening of the reflections of XRPD patterns, suggesting that the excess oxygen destroys partially the ordering of the trigonal lattice.

Conclusions

These numerous studies of the “114” cobaltites and ferrites show the extraordinary wealth of these systems, due to the great flexibility of their structure and of the valency of the transition element. As a consequence, many closely related structures and order-disorder phenomena, dealing with the oxygen stoichiometry remain to be discovered. The magnetic properties of those purely tetrahedral structures are of great interest. One example deals with the spin glass behaviour of the cubic $\text{LnBaFe}_4\text{O}_7$, which probably originates from the tetrahedral framework $[\text{Fe}_4]_\infty$ similar to that observed in pyrochlore oxides. Another example concerns the issue of ferrimagnetism or of ferromagnetism associated to geometric frustration in the same structure for the trigonal and orthorhombic phases, bearing in mind that such structures offer two sublattices for the transition metal element. These results open the route to the exploration of new phenomena in the field of magnetic frustration.

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Figure captions

Fig. 1 : Trigonal structure of $\text{LnBaCo}_4\text{O}_7$ and $\text{CaBaFe}_4\text{O}_7$: (a) hexagonal close packed “ BaO_3 ” layer parallel to (001), (b) hexagonal “ABCB” (hchc) close packing of “ BaO_3 ” and “ O_4 ” layers, (c) Perspective view for the trigonal structure nearly along $\langle 1-10 \rangle_{\text{H}}$ showing the alternate stacking of the kagome (K) and triangular layers (T) of CoO_4 (or FeO_4) tetrahedra, (d) view of the structure along $\langle 1-10 \rangle_{\text{H}}$ showing large distorted tunnels running along this direction.

Fig 2. Zero field cooled (ZFC) and field cooled (FC) magnetization curves of YBaCo_4O_7 registered with a magnetic field of 50mT after M. Valldor and H. Andersson [3]

Fig. 3: Seebeck coefficient as a function of T for YBaCo_4O_7 , $\text{YbBaCo}_4\text{O}_7$ and $\text{Y}_{0.5}\text{Yb}_{0.5}\text{BaCo}_4\text{O}_7$. The T_{S} values, taken on the S(T) curves collected on cooling, as a function of the rare-earth ionic radius, are shown in the inset.

Fig. 4: T-dependent Seebeck (S) coefficient curves of (a) $\text{YBaCo}_{4-x}\text{Zn}_x\text{O}_7$ with $x=0, 0.2, 0.3$, (b), $\text{YBaCo}_{4-x}\text{Al}_x\text{O}_7$ with $x=0, 0.2$.

Fig. 5. Structure of $\text{CaBaCo}_4\text{O}_7$, showing the buckling of the kagome layers: (a) view along a, (b) view along c.

Fig. 6. $\text{CaBaCo}_4\text{O}_7$: (left axis) Magnetization versus temperature, registered under 0.3 T (right axis) $\chi^{-1}(\text{T})$ curve from which the large Curie-Weiss constant and the abnormally high magnetic moment ($6,8 \mu_{\text{B}}$) of this material are obtained.

Fig. 7. ac- $\chi(\text{T})$ curves of $\text{CaBaCo}_4\text{O}_7$ [χ' real part (left axis) and χ'' imaginary part (right axis)] collected for $f = 10^4$ Hz and $\mu_0 H = 10^{-3}$ T.

Fig. 8. Isothermal magnetization of $\text{CaBaCo}_4\text{O}_7$ registered at 5 K and 100 K.

Fig. 9: Magnetization M(T) curve of $\text{CaBaFe}_4\text{O}_7$: zero field cooled (ZFC) in solid symbol and field cooled (FC) in open symbol.

Fig. 10: Magnetic field dependence of the magnetization, M(H) for $\text{CaBaFe}_4\text{O}_7$ at 5K.

Fig. 11: Structure of YBaFe_4O_7 : (a) Perspective view of the cubic nearly along $\langle 111 \rangle_{\text{C}}$ showing the Fe_4O_7 framework, (b) View along $\langle 110 \rangle_{\text{C}}$ direction (c) “ABCABC” (ccc) cubic close packing of “ O_4 ” and “ BaO_3 ” layers.

Fig. 12: YBaFe_4O_7 : (a) (left y-axis) T-dependence of the magnetic susceptibility χ ($=M/H$) collected according to zero-field-cooling (ZFC) and field-cooling (FC) processes ($\mu_0 H = 0.3$ T); (right y-axis) corresponding T-dependent reciprocal magnetic susceptibility (χ^{-1}) from ZFC $\chi(\text{T})$ curve. (b) T-dependence of the real part of the ac- χ

measured at 2 frequencies for the excitation magnetic field ($\mu_0 H = 10^{-3}$ T). An enlargement in the T region of the χ' maximum is given in the upper right region.

Fig. 13. TG curves for as-synthesized $\text{LnBaCo}_4\text{O}_{7+\delta}$ samples ($0.03 < \delta < 0.14$) recorded in O_2 gas flow with a heating rate of $1^\circ\text{C}/\text{min}$. The two humps at about $200\text{--}400^\circ\text{C}$ and above 600°C are due to oxygen absorption/desorption and phase decomposition, respectively. After S. Kadota et al. [26].

Fig. 1 : Trigonal structure of $\text{LnBaCo}_4\text{O}_7$ and $\text{CaBaFe}_4\text{O}_7$: (a) hexagonal close packed “ BaO_3 ” layer parallel to (001), (b) hexagonal “ABCB” (hchc) close packing of “ BaO_3 ” and “ O_4 ” layers, (c) Perspective view of the trigonal structure nearly along $\langle 1-10 \rangle_{\text{H}}$ showing the alternate stacking of the kagome (K) and triangular layers (T) of CoO_4 (or FeO_4) tetrahedra, (d) view of the structure along $\langle 1-10 \rangle_{\text{H}}$ showing large distorted tunnels running along this direction.

Fig 2. Zero field cooled (ZFC) and field cooled (FC) magnetization curves of YBaCo₄O₇ registered with a magnetic field of 50mT after M. Valldor and H. Andersson [3]

Fig. 3: Seebeck coefficient as a function of T for YBaCo_4O_7 , $\text{YbBaCo}_4\text{O}_7$ and $\text{Y}_{0.5}\text{Yb}_{0.5}\text{BaCo}_4\text{O}_7$. The T_S values, taken on the $S(T)$ curves collected on cooling, as a function of the rare-earth ionic radius, are shown in the inset.

Fig. 4: T-dependent Seebeck (S) coefficient curves of (a) $\text{YBaCo}_{4-x}\text{Zn}_x\text{O}_7$ with $x=0, 0.2, 0.3$, (b) $\text{YBaCo}_{4-x}\text{Al}_x\text{O}_7$ with $x=0, 0.2$.

Fig. 5. Structure of $\text{CaBaCo}_4\text{O}_7$, showing the buckling of the kagome layers: (a) view along a , (b) view along c .

Fig. 6. $\text{CaBaCo}_4\text{O}_7$: (left axis) Magnetization versus temperature, registered under 0.3 T (right axis) $\chi^{-1}(T)$ curve from which the large Curie-Weiss constant and the abnormally high magnetic moment ($6,8 \mu_B$) of this material are obtained.

Fig. 7. ac- $\chi(T)$ curves of $\text{CaBaCo}_4\text{O}_7$ [χ' real part (left axis) and χ'' imaginary part (right axis)] collected for $f = 10^4$ Hz and $\mu_0 H = 10^{-3}$ T.

Fig. 8. Isothermal magnetization of $\text{CaBaCo}_4\text{O}_7$ registered at 5 K and 100 K.

Fig. 9: Magnetization $M(T)$ curve of $\text{CaBaFe}_4\text{O}_7$: zero field cooled (ZFC) in solid symbol and field cooled (FC) in open symbol.

Fig. 10: Magnetic field dependence of the magnetization, $M(H)$ for $\text{CaBaFe}_4\text{O}_7$ at 5K.

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