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Complex ~~m~~Magnetic ~~b~~Behavior in the ~~n~~Novel C~~c~~obaltite $YBaCo_4O_7$

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Resumen

El comportamiento magnético de muestras policristalinas de la nueva cobaltita $YBaCo_4O_7$ fue estudiado por magnetometría SQUID. A pesar de que las interacciones de intercambio entre los iones de Co muestran un carácter predominantemente antiferromagnético, la componente ferromagnética pareció ser lo suficientemente fuerte como para ser detectada, aún a temperatura ambiente. Mediciones SQUID mostraron la presencia de orden ferromagnético débil a temperatura ambiente con saturación aparente de $4x10^{-3}$ μ_B/Co ($1.5x10^{-2}$ μ_B/Co a 5 K) en un campo magnético externo de 1 T. Indicación del orden ferromagnético a temperatura ambiente fue también observada mediante la medición de la dependencia de la magnetización con la temperatura en campos magnéticos débiles. Curiosamente, transición a un estado antiferromagnético fue evidenciada a una temperatura de ~250 K cuando la muestra fue enfriada en campo cero (ZFC). Estas observaciones sugieren que el comportamiento magnético de este material es no trivial. Probablemente, este comportamiento puede interpretarse como tipo vidrio de espín con una componente ferromagnética. Sin embargo, la señal ferromagnética observada en este material a 300 K parece ser originada por la presencia de una fase secundaria que con probabilidad alta se trata de la fase $YBaCo_2O_{5.5}$ la cual es ferromagnética a temperatura ambiente.

Palabras claves: Cobaltitas, ~~R~~reacción en estado sólido, ~~P~~propiedades magnéticas.

Abstract

~~The~~ ~~m~~Magnetic behavior of polycrystalline samples of the new cobaltite $YBaCo_4O_7$, were carefully studied by SQUID magnetometry. In spite of the predominant antiferromagnetic character of ~~the~~ exchange interactions between cobalt ions, a ferromagnetic component seemed to be strong enough as to be detected still at room temperature. Certainly, SQUID measurements showed weak ferromagnetic ordering at room temperature, with an apparent magnetic saturation of $4x10^{-3}$ μ_B/Co ($1.5x10^{-2}$ μ_B/Co at 5 K) in an external magnetic field of 1 T. Indication of ferromagnetic ordering at RT was also observed, by measuring ~~the~~ dependence of magnetization on ~~the~~ temperature in weak magnetic fields. Curiously, a transition to an antiferromagetic state was evident at a temperature as high as 250 K, in the zero-field cooling procedure. These findings suggest~~ed~~ that ~~the~~ magnetic behavior of the studied compound is far from trivial. Probably, ~~the ferromagnetc~~ it may be interpreted as a spin glass-like state with a weak ferromagnetic component. Nevertheless, the ferromagnetic signal detected in this material at 300 K, seems to be originated by the presence of a secondary phase. It is highly probable the secondary phase to be the $YBaCo_2O_{5.5}$ which, certainly, is ferromagnetic at tempertatures close to 300 K.

Keywords: Cobaltite, ~~S~~solid ~~S~~state ~~R~~reaction, m~~M~~agnetic properties.

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1. Introduction

Recently, cobalt-containing oxide phases have attracted a considerable attention due to their valuable properties, including a high level of oxygen ionic, and electronic conductivity [1-3], high catalytic and electrocatalytic activity [3], magnetic ordering [4,5], and superconductivity phenomenon [6].Thus, studies on new cobaltite-based materials with improved functional characteristics ~~is~~are a very important issue. In recent years, a new class of complex oxides with a common chemical formula $LnBaCo_4O_7$ (Ln = lanthanoid or Y) were synthesized [7,8]. ~~The c~~Crystal structure of these compounds, firstly reported for $HoBaCo_4O_7$ [7], was found to be similar to hexagonal $Ba_2Er_2Zn_8O_{13}$ [9]. This lattice comprises layers formed by two different types of cobalt-oxygen tetrahedra, $(Co1)O_4$ and $(Co2)O_4$, which are connected by corners, and characterized by different bond lengths. Such a feature was interpreted as favoring actual ordering of ~~the~~ cobalt cations in different oxidation states [7]. ~~The l~~Long-range charge ordering between $Co2^+$ and $Co3^+$ ions, below 210–220 K, and its influence on physical properties were reported earlier for another family of layered cobaltites, $LnBaCo_2O_5$ (Ln =Y, Tb, Dy, Ho) [10,11]. Because ~~the~~of crystal field energy differs little from the intratomic exchange energies in crystals containing Co ions, the latter may reside in different spin states depending on ~~the~~ actual external conditions (temperature and pressure) [12]. For instance, Co+ ions may exist in the low-spin (LS, S=0 $t_{2g}^6\varepsilon_g^0$), intermediate-spin (IS, S=1 $t_{2g}^5\varepsilon_g^1$), and high-spin (HS, S=2 $t_{2g}^4\varepsilon_g^2$) states. It is the layered 2D structure of ~~the~~ double cobaltites, and the different spin states of Co ions ~~t~~what account for the rich diversity of properties of this class of compounds [12].

In this work, ~~the~~ synthesis and characterization of new mixed-valence cobalt oxide $YBaCo_4O_7$, ~~is~~are reported. Special attention is devoted to ~~the~~ magnetic response of this compound at high temperatures.

2. Experiment

Powders of $YBaCo_4O_7$ (YBCoO) were obtained from stoichiometric mixtures of Y_2O_3, $Ba(CH_3COO)_2$, and Co_2O_3 reactants. After mixing ~~the~~all constituents thoroughly in an agate mortar, the resulting powder was slowly heated in air (~ 5 °C/min) up to 1200 °C, and it was calcined for 48 h. After this process was accomplished, the sample was cooled slowly inside ~~the~~a furnace at~~o~~ ambient temperature. No reaction occurred between Co, and ~~the~~ ~~p~~Pt crucible, as it was corroborated by X-ray diffraction (XRD). The black single phase YBCoO powder was grounded, and then pressed into pellets (~3 cm in diameter and thickness ~3 mm) which were finally sintered at 1300 °C for 11 hours in air. The so fabricated YBCoO powders, were characterized after their structural, morphological, and magnetic properties employing X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) and SQUID (Quantum Design) magnetometry, respectively.

3. Results and discussion

The XRD results (Fig.1) indicate that YBCoO powder samples are prodominatly single phase with hexagonal crystal structure (space group $P6_3mc$). The lattice parameters obtained by the Rietveld refinement resulted to be a=6.3057 Å and c=10.2546 Å, which are very close to those reported in the literature for this compound [8]. The EDS analysis of this sample (not shown) shows no traces of foreign atoms as Pt which might stem from the Pt crucible used for the calcination. The evaluation of the EDS spectra resulted, in cationic composition $Y_1Ba_{1.001}Co_{3.97}O_x$, in agreement with the nominal one in the limit of experimental errors.

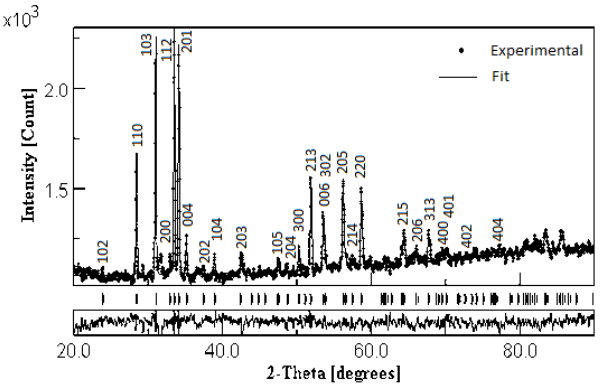

Fig. 1. X-ray diffraction pattern of an $YBaCo_4O_7$ powder sample calcined at 1200 °C for 48 h. The Rietveld pattern is indicated by the solid line.

Although the DRX pattern does not show additional reflections stemming from a secondary phase, the presence of such phases may not be ruled out based only on the DRX results. The DRX is a bulk analytical technique which would hardly detect small molar concentrations of impurities. It is known that 114 cobaltites are notoriously difficult to prepare. During the synthesis, the phases $YBaCo_2O_{5.5}$ and $YBaCo_2O_{5.44}$ may form easily. A small amount of such impurities would be hard to pick up without ~~the~~ help of high resolution neutron diffraction (XRD does not see O very well when it is part of a sample containing much heavier elements). Although, the DRX analysis provides no clear evidence of ~~the presence~~ a secondary phase presence, sensible magnetic measurements shows that the samples are certainly affected by $YBaCo_2O_{5.5}$ which is ferromagnetic at ~300 K. A similar result was reported for $YBaCo_4O_7$ single crystals [14], for which the 112 phase content came out to be ~2%.

Shown in Fig. 2, is a SEM micrograph of an $YBaCo_4O_7$ polycrystalline simple after reacting the powders at 1200 °C in air for 48 hours, using a Pt crucible followed it by slow cooling at~~o~~ room temperature. Hexagonal-like prisms of different sizes are readily recognized on this micrograph. Statistical analysis of the grain size based on the large area image yielded an average grain size of 4.5 μm.

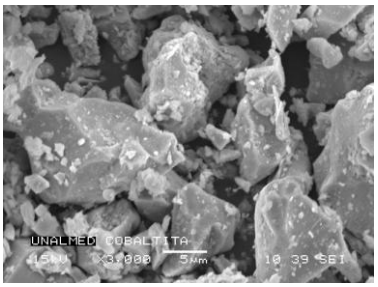

Fig. 2. SEM image of an$YBaCo_4O_7$ powder sample showing the hexagonal form of the crystallites.

~~The f~~Field dependence of ~~the~~ magnetization was measured at different temperatures (Fig. 3). Interestingly, the $M(H)$ dependence shows a well defined hysteretic behavior at room temperature with a magnetic saturation of $4x10^{-3}$ μ_B/Co in a field $\mu_0 H$~1 T. This value increased up to $1.5x10^{-2}$ μ_B/Co at 5 K. Such values for the magnetization are too small for the ferro- or ferrimagnetic states. It is very probable that the ferromagnetic signal at 300 K is originated by the secondary phase $YBaCo_2O_{5.5}$, as this phase shows a ferromagnetic behavior in a narrow temperature window (~20 K) below T_C (~300 K) [15]. Nevertheless, at temperatures as low as 10 K, the $M(H)$ curve measured on this phase shows a typical behavior of an antiferromagnetic material. The molar fraction of $YBaCo_2O_{5.5}$, originating the magnetic signal at 300 K, should be too small to be detected by normal XRD measurements.

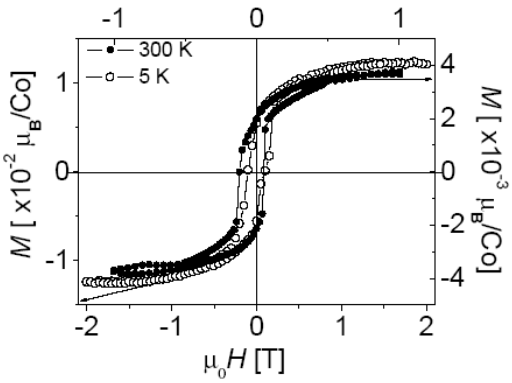

Fig. 3. Field dependence of the magnetization of an $YBaCo_4O_7$ powder sample measured at 5 K and 300 K.

~~The z~~Zero-field cooling (ZFC), and field cooling (FC) dependence of the magnetization on ~~the~~ temperature, was recorded in several field strengths in order to better appreciate ~~the~~ possible different transitions in this system. The ZFC curve (presented in Fig. 4), shows a strong increase in the magnetization at 300 K with an apparent saturation at ~200 K. This behavior resembles that displayed by a ferromagnetic substance with a well defined Curie temperature [13]. Nevertheless, at T<200 K, M increases monotonically up to ~30 K characterizing a paramagnetic state. A conspicuous rise in M comes about at T<30 K. In turn, the temperature dependence of the magnetization obtained in a FC procedure shows a special feature at ~250 K, which seems to correspond to a transition to an antiferromagnetic state. This feature should be associated with the $YBaCo_2O_{5.5}$ foreign phase.

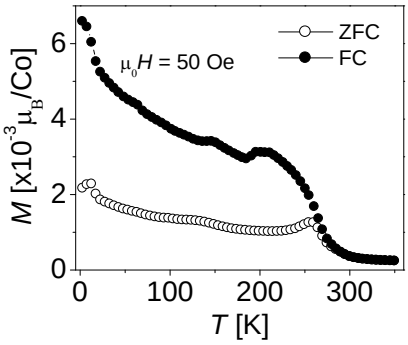

Fig. 4. Dependence of the ZFC and FC magnetization of an $YBaCo_4O_7$ powder sample on temperature. The measuring fiel amounted to 50 Oe.

One general feature of the magnetization in $YBaCo_4O_{7+\delta}$ is a pronounced thermo-magnetic irreversibility. ~~The d~~Data taken upon cooling the sample in a magnetic field (FC), differed from those obtained on heating after the sample was cooled in zero field (ZFC) (Fig. 4). Quite often such magnetic irreversibility observed in transition-metal oxides is attributed, sometimes without due care, to the formation of a spin-glass state. It should be noted, however, that the idea of a spin glass implies that no long-range (or intermediate-ranged order) is developed in ~~the~~a spin system [16]. The divergence of FC and ZFC curves seemed, nevertheless, reflecting spin-glass freezing as the peak in the real part of the ac susceptibility exhibited very little or no frequency dependence (Fig. 5). Note that in the case of $YBaCo_4O_{7+\delta}$, the magnetic irreversibility shows up only below the temperature onset of a ferromagnetic-like behavior of the $YBaCo_2O_{5.5}$ phase. Thus, the magnetic irreversibility is most likely associated with a conventional ferromagnetic domain structure or with a metamagnetic transition [17].

The noticiable magnetic behavior of the sample at ~250 K, when is measured in a ZFC procedure, was corroborated by measuring the ac susceptibility as a function of the temperature and the frequency. As it is shown in Fig. 5, a well defined peak is observed in the real component of the susceptibility at ~250 K, which is practically frequency independent. As it was stated above, the peak at ~250 K in the susceptibility curve should be stem from the $YBaCo_2O_{5.5}$ phase.

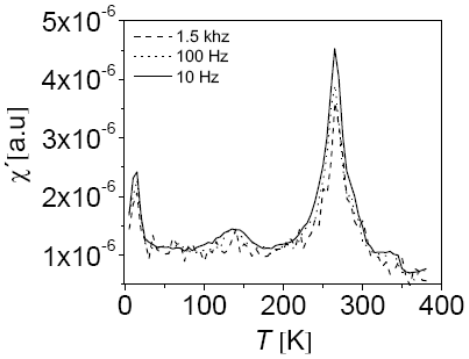

Fig. 5. Temperature dependence of the real component of the ac susceptibility measured on an $YBaCo_4O_7$ powder sample. The data were recorded at various frequencies.

The latter findings suggest that the magnetic behavior of such Co-based compounds is complex. Probably, the magnetic behavior of this compound may be interpreted as a spin glass-like state with a weak ferromagnetic component. Nevertheless, the effect of secondary phases in cobaltites on the ferromagnetic response should not be discarged. In this way, further work is necessary in order to get a ~~i~~deeper insight into the complex magnetic configuration of these novel oxides.

4. Conclusions

Polycrystalline samples of the new cobaltite $YBaCo_4O_7$ were obtained through standard solid state reaction, ~~u~~and their structural, morphological, and magnetic properties carefully studied. X-ray powder diffraction pattern showed reflexes corresponding only to a pure hexagonal structure. In spite of this result, the presence of secondary phases should not be excluded. Careful SQUID measurements showed weak ferromagnetic ordering at room temperature with a magnetic saturation of $4x10^{-3}$ μ_B/Co which~~,~~; nevertheless, seemed to be due to the $YBaCo_2O_{5.5}$ phase. Well defined hysteresis was also observed at 5 K with a magnetic saturation of ~~(~~$1.5x10^{-2}$ μ_B/Co. In principle, the magnetic behavior of the compound at low tempertures may be interpreted as a spin glass-like state with a weak ferromagnetic component.

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