

Synthesis and magnetic properties of the double layer perovskite $\text{CeBaFe}_2\text{O}_{5+w}$

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The synthesis, crystallographic structure, and magnetic properties of polycrystalline single-phase samples of $\text{CeBaFe}_2\text{O}_{5+w}$ are reported. An orthorhombic structure belonging to the $Pmmm$ space group was identified through Rietveld analysis of x-ray diffraction data. The room temperature lattice parameters were found to be $a=3.9666(1)$ Å, $b=3.9314(1)$ Å, and $c=7.8291(1)$ Å. A sudden change in magnetization at the temperature of 130 K was attributed to a Verwey-type transition, and a broader change at 220 K was attributed to a Verwey premonitory transition, as expected in the $R\text{BaFe}_2\text{O}_{5+w}$ compounds (R =rare earth). At a much higher temperature, a paramagnetic to ferromagneticlike transition was observed around 600 K. © 2010 American Institute of Physics. [doi:10.1063/1.3359436]

Perovskite-type structures have been attracting huge attention due to their interesting physical properties, mainly produced by peculiar competitions involving charge, spin, and orbital degrees of freedom.¹⁻³ Also, the valence-state mixing, charge separation, and spatial ordering in condensed matter systems have received considerable attention.^{4,5} The first model on valence-state ordering transition was presented by Verwey,^{6,7} to explain simultaneous abrupt changes in conductivity and crystallographic structure observed in Fe_3O_4 , although many questions still remain unsolved in this area.⁸ In Verwey's model, above the transition point (T_V), the ions Fe^{2+} and Fe^{3+} would be randomly distributed over the Fe sites, allowing relatively easy valence exchange by means of thermally activated electron hopping. By cooling below T_V , charge ordering then would occur, with the ions Fe^{2+} and Fe^{3+} going alternately to parallel lattice planes.

More recently a Verwey-type mixed-valence-state was observed in Ref. 9 $\text{EuBaFe}_2\text{O}_{5+w}$, with $T_V \approx 256$ K, as well as in other rare earth (R) substitutions of the $R\text{BaFe}_2\text{O}_{5+w}$ double-perovskite system.³ Especially, much interest has been devoted to explain the electronic and magnetic structures of YBaFe_2O_5 , with $T_V \approx 309$ K, through theoretical studies.^{10,11} However, until now, the compound with $R=\text{Ce}$ was not reported as a stable and feasible system. Here, we will be presenting the first results on the successful preparation and characterization of polycrystalline $\text{CeBaFe}_2\text{O}_{5+w}$ samples.

Ideal perovskites have the general formula ABO_3 . This structure can be visualized as a cubic lattice with the A atoms at the corners, the O atoms at the face centers, and the B atoms in the center of the cell. The basic double-perovskite structure is generated by introducing another ion (B') in half of the B positions, yielding the basic double-perovskite

structure formula $\text{A}(2)\text{BB}'\text{O}(6)$. Our results on the double-perovskite system $\text{CeBaFe}_2\text{O}_{5+w}$ will be discussed in the next sections.

We have prepared the $\text{CeBaFe}_2\text{O}_{5+w}$ samples following a solid phase reaction method, starting with a stoichiometric mixture of $\text{CeO}_2 + \text{BaCO}_3 + \text{Fe}_2\text{O}_3$ powders. Next, the powder mixture was pressed into a cylindrical shape, which was annealed at 930 °C for 24 h in an atmosphere of 96% Ar + 4% H_2 . Next, the sintered pellet was milled into a fine powder that was analyzed by x-ray powder diffraction ($\text{Cu } K\alpha$ radiation) at room temperature, in order to monitor the perovskite phase formation. This cycle was repeated at least four times until the pure phase was obtained. Then, a Rietveld analysis, using the program DBWS98, was done on the x-ray diffraction (XRD) data obtained for a pure phase sample (see Fig. 1). In our best sample, the Rietveld refinements indicated a single phase with orthorhombic crystalline

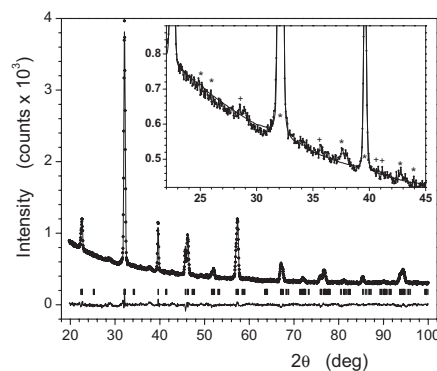


FIG. 1. XRD pattern for $\text{CeBaFe}_2\text{O}_{5+w}$, measured at room temperature with $\text{Cu } K\alpha$ radiation. The solid line represents a Rietveld fit to the data, using an orthorhombic structure with space group $Pmmm$. The inset shows a magnified region that reveals some impurity peaks marked with stars for BaCO_3 and crosses for BaCeO_3 . Notice the coincidence of peak positions for $\text{CeBaFe}_2\text{O}_{5+w}$ and BaCO_3 at $2\theta=32.17^\circ$ and 39.53° .

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TABLE I. Parameters determined from Rietveld analysis of XRD data for a $\text{CeBaFe}_2\text{O}_{5+w}$ sample. The best fit was obtained for an orthorhombic structure (space group $Pmmm$), with lattice parameters $a=3.9666(1)$ Å, $b=3.9314(1)$ Å, and $c=7.8291(1)$ Å. Thermal parameters (B_{iso}) for all oxygen were kept fixed during the fitting procedure; n is the occupancy factor; $R_{\text{wp}}=3.0\%$; $R_{\text{expect}}=4.6\%$. The fitting uncertainties appear in parentheses.

Ion	Site	x	y	z	B_{iso}	n
Ce	1c	0	0	1/2	0.54(7)	1.0
Ba	1a	0	0	0	1.23(7)	1.0
Fe-1	2t	1/2	1/2	0.254(4)	0.75(13)	0.693(4)
Fe-2	2t	1/2	1/2	0.25	0.75(13)	0.306(4)
O-1	1f	1/2	1/2	0	0.92	1.0
O-2	2s	1/2	0	0.290(6)	0.92	1.0
O-3	2r	0	1/2	0.313(4)	0.92	1.0
O-4	1h	1/2	1/2	1/2	0.92	0.380

structure (space group $Pmmm$) and an impurity content smaller than 2%. This value was obtained by adding the estimated content of two possible impurities, BaCO_3 (Ref. 12) and BaCeO_3 ,¹³ both nonmagnetic, whose peaks are marked by stars and crosses, respectively, in the inset of Fig. 1. The amount of each impurity phase is roughly below 1%, calculated by the ratio between the heights of the most intense XRD peaks from the impurity and principal ($\text{CeBaFe}_2\text{O}_{5+w}$) phases.

The main obtained parameters are shown in Table I, and the lattice parameters were found to be $a=3.9666(1)$ Å, $b=3.9314(1)$ Å, and $c=7.8291(1)$ Å. In Table I, n is the occupancy factor and the fitted uncertainties appear in parenthesis. The thermal parameters (B_{iso}) for the oxygen ions were kept fixed during the fitting procedure, following previous works on the $\text{RBaFe}_2\text{O}_{5+w}$ system.^{14,15} The agreement factors were $R_{\text{wp}}=3.0\%$ and $R_{\text{expect}}=4.6\%$. The unusual value of R_{wp} (below R_{expect}) (Ref. 16) possibly indicates the necessity of reducing the angular steps to values smaller than 0.05° , which was employed in our measurements. Following a model described in Ref. 15, about 70% of Fe-1 ion is located in site B (square-pyramidal site) and about 30% of Fe-2 ion is in site B' (octahedral site). The occupancy of the site 1h can provide a rough evaluation of the oxygen excess per formula unit $w \approx 0.380$, which is a suitable value for samples reacted in oxygen-rich atmospheres.¹⁵ However, this result needs a confirmation through more precise methods, like chemical titration or Rietveld analysis on neutron diffraction data.

Another Rietveld data refinement, using an orthorhombic structure in the space group $Pmna$, also gives acceptable results with $R_{\text{wp}}=2.9\%$ and $R_{\text{expect}}=4.7\%$. However, this structure is expected to be stable only at low temperatures,⁹ or when just Fe^{3+} ions are present in the $\text{CeBaFe}_2\text{O}_{5+w}$ sample, which implies $w=0.5$ by assuming the presence of only Ce^{3+} and Ba^{2+} ions. However, in this ordered structure no Verwey transition is expected to occur, according to the model of electron hopping between Fe^{2+} and Fe^{3+} ions.¹⁷ To help clarify this point, x-ray measurements taken at low temperatures (e.g., 10 K) would be very useful. Finally, we would like to add that a Rietveld refinement using tetragonal structure, space group $P4/mmm$, was also done with no sat-

isfactory results ($R_{\text{wp}}=6.2\%$ and $R_{\text{expect}}=4.7\%$). Therefore we can exclude this possibility, at least for the presently studied Ce-based samples.

A chemical characterization was done through scanning electron microscopy with energy dispersive x-ray (SEM-EDX) analysis. The evaluated contents (in at. %) for the metallic elements were Fe:Ba:Ce=48.43:26.88:24.69. We notice that these atomic proportions are reasonably in good agreement with the $\text{CeBaFe}_2\text{O}_{5+w}$ stoichiometry, with an excess of around 1.2% and 0.2% per formula unit for Ba and Ce, respectively. This total excess of about 1.4% is consistent with the total amount of impurities, evaluated through XRD data to be below 2%.

Magnetic characterization was performed by measuring magnetization curves as a function of temperature at a fixed magnetic field (M versus T), and magnetization as a function of applied magnetic field at a fixed temperature (M versus H). A superconducting quantum interference device magnetometer MPMS-5T from Quantum Design, with oven option (2–800 K) has been employed. Here we only show M versus T curves, in the temperature range of 2–380 K (Fig. 2) and 300–800 K (Fig. 3).

The overall behavior of the zero field cooling (ZFC) and field cooling (FC) curves, shown in Fig. 2, suggests a possible mixture of different magnetic phases, although no magnetic impurities were identified in the sample. A narrow and large increase, which reminds an antiferromagnetic (AFM) to ferromagnetic (FM)-like transition, occurs at $T_V \approx 130$ K in

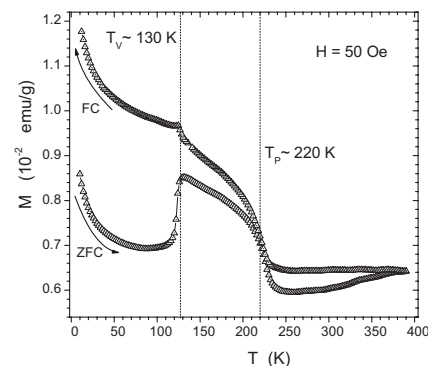


FIG. 2. Magnetization as a function of temperature, measured under $H=50$ Oe, showing a narrow transition at T_V (Verwey transition) and a broader transition at T_P (premonitory transition).

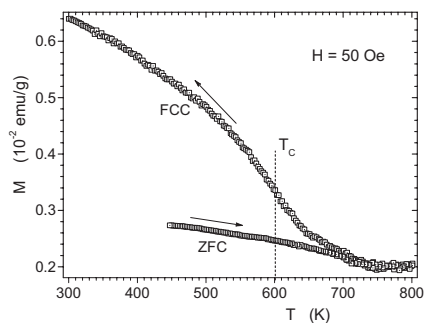


FIG. 3. Magnetization as a function of temperature, measured under $H = 50$ Oe, showing a broad change around $T_C = 600$ K, attributed to a paramagnetic to ferromagneticlike phase transition.

the ZFC curve. This is interpreted as a possible Verwey-type transition, with the Fe^{2+} and Fe^{3+} ions becoming ordered below T_V . This transition is also observed in the FC curve, although the FM-like to AFM transition appears almost suppressed. This irreversibility could eventually be explained within the hypothesis of phase separation that involves a mixture of FM-like and AFM domains of short range order, typical in perovskite systems.^{5,18,19} Thus, a FC process could favor a more aligned configuration of FM-like domains that produces a larger magnetization, contrasting with a disordered configuration of FM-like domains in the ZFC process. At around 220 K there is a transition (maximum slope) from a weaker to a stronger FM-like phase, when lowering T , for both ZFC and FC curves. We interpret this feature as a possible premonitory transition (T_p), where two intermediate valence-states ($\text{Fe}^{2.5+\epsilon}$ and $\text{Fe}^{2.5-\epsilon}$) start evolving gradually toward the fully ordered state at T_V .²⁰ Finally, at much higher temperatures (Fig. 3), it seems that a broad FM-like to paramagnetic transition occurs, with $T_C \approx 600$ K determined at the maximum slope point.

It is known that T_V decreases from ~ 300 to ~ 200 K and T_p decreases from ~ 325 to ~ 285 K, when the rare earth ionic radii increases from 1.155 \AA ($R = \text{Ho}$) to 1.250 \AA ($R = \text{Nd}$) in the $R\text{BaFe}_2\text{O}_{5+w}$ compounds.³ Assuming that the Ce^{3+} ion is present in $\text{CeBaFe}_2\text{O}_{5+w}$ with an ionic radii of 1.283 \AA ,²¹ which is about 26% higher than the Nd radii, one should then expect a larger decrease in T_V and T_p if the same underlying mechanism is preserved. Therefore, based on this reasoning, the observed $T_V \approx 130$ K and $T_p \approx 220$ K seem to attain plausible values. These values of T_V and T_p are the lowest reported so far, for a compound in the $R\text{BaFe}_2\text{O}_{5+w}$ system.

In the phase separation hypothesis the magnetic ions are typically in a mixed-valence-state.^{19,22} Therefore, in principle, it could be possible to have magnetic Ce^{3+} and non-magnetic Ce^{4+} ions in different regions of the sample. This would imply an inhomogeneous system with the presence also of Fe^{3+} and Fe^{2+} ions, eventually requiring local variations in the oxygen stoichiometry. However, it seems that only trivalent states of the rare earth ions (R^{3+}) have been observed in $R\text{BaFe}_2\text{O}_{5+w}$ compounds that exhibit the Verwey transition.^{3,9,15} In order to clarify the occurrence and effects of possible phase separation in this system, particularly in the $\text{CeBaFe}_2\text{O}_{5+w}$ compound, more work is still underway.

We have made the synthesis, as well as the structural and magnetic characterization of the double layer perovskite compound $\text{CeBaFe}_2\text{O}_{5+w}$. XRD analysis, using the Rietveld method, is in good agreement with an orthorhombic structure (space group $Pmmm$) with lattice parameters $a = 3.9666(1) \text{ \AA}$, $b = 3.9314(1) \text{ \AA}$, and $c = 7.8291(1) \text{ \AA}$. About 70% of Fe-1 ion type is located in site B (square-pyramidal site) and about 30% of Fe-2 ion type is in site B' (octahedral site). The occupancy of site 1h gives a qualitative information about the oxygen excess per formula unit, $w \approx 0.380$, although this value requires a confirmation by other methods.

Magnetization curves (M versus T and M versus H) in the ranges of $2 \text{ K} \leq T \leq 800 \text{ K}$ and $50 \text{ kOe} \leq H \leq 50 \text{ kOe}$ suggest a possible mixture of magnetic phases in our $\text{CeBaFe}_2\text{O}_{5+w}$ sample. We determined a Verwey-type transition temperature ($T_V \approx 130$ K), a possible premonitory Verwey transition temperature ($T_p \approx 220$ K), and a Curie temperature ($T_C \approx 600$ K) that separates the paramagnetic and ferromagneticlike states.

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