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Structural disorder effect on the structural and magnetic properties of $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ manganites (Re = Pr, Sm, Eu, Gd, Dy and Ho)

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ABSTRACT

The influence of the A-site cation size-disorder σ^2 on the structural and magnetic properties of the polycrystalline $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ (Re = Pr, Sm, Eu, Gd, Dy and Ho) samples with a constant average ionic radius $< r_A > = 1.2445$ Å, is investigated. All samples were synthesized using the solid-state reaction. Rietveld refinement of the X-ray diffraction patterns shows that the substitution generates a structural transition from tetragonal to orthorhombic symmetry. The temperature dependence of magnetization indicates a weakening of ferromagnetism by the increase of σ^2. The large difference between the field cooled and zero field cooled magnetization below Curie temperature suggests the presence of an inhomogeneous mixture of a ferromagnetic and antiferromagnetic domains at low temperature. The maximum of the magnetic entropy change decreases with increasing the mismatch effect. However, several peculiarities were observed in the magnetic behavior indicating that σ^2 is not the only factor controlling the physical properties; the nature and the magnetic moment of the substituent should be taken in consideration.

1. Introduction

The Half doped manganites with general formula $Re_{0.5}Ae_{0.5}MnO_3$ (Re = La, Pr, Nd, Sm,... and Ae = Sr, Ca, Ba...) were widely studied in the last decades. These compounds present many interesting structural, electrical and magnetic properties such as the colossal magnetoresistance and the magnetocaloric effect, which can explain their importance in the scientific research field [1–6]. These series of manganites present a Mn^{3+}/Mn^{4+} ratio equal to 1 which gives them some unique properties like charge ordering, phase separation (PS) as well as the presence of several magnetic transitions. Recent studies have indicated that the physical properties of these compounds are highly sensitive to many factors, like the average ionic radius of the A-site $< r_A >$, the cationic disorder at the A-site given by $\sigma^2 = \sum_i y_i r_i^2 - < r_A >^2$, the doping level and the oxygen deficiency...[7–9]. The variance σ^2 quantifies the random disorder of cations distributed over the A site of manganites. Recent results have shown that the crystallographic structure of these materials depends on disorder. For the high values of $< r_A >$ (1.24 Å–1.30 Å), the structure shifts from the orthorhombic to the rhombohedric system when the disorder increased. On the other hand, for the low values of $< r_A >$ (1.18 Å–1.24 Å) the structure keeps the orthorhombic system whatever the value of disorder is [10,11]. The structural disorder highly affects magnetic properties due to the correlation between structure and magnetism in manganites. The variation of the Mn-O-Mn bond angle leads to a random distribution of the exchange interactions. The important effect of σ^2 on magnetic properties was demonstrated by the study of different manganites where $< r_A >$ was fixed [12–14]. This parameter has also an effect on the temperature of the magnetic transitions. Rodriguez-Martinez and Attfield have shown that the increase of σ^2 leads to a lowering of the Curie temperature T_C [13]. Thus, for the same value of $< r_A >$, the compound with a high disorder value has a lower T_C. σ^2 induces a local disorder within the structure, which tends to decrease the intensity of magnetic interactions and affects the stability of ferromagnetic (FM) and antiferromagnetic (AFM) state in these compounds.

In addition, the strong competition between the double exchange and super exchange mechanisms and the presence of disorder leads to a microscopic PS in the half doped manganites. The PS phenomenon has been intensively studied in these compounds [15–17]. This phenomenon is manifested by a coexistence of different magnetic phases. Theoretically, one of the possible origins to understand the existence of PS is the existence of a transition possessing percolative characteristics: it is an order-disorder transition, which is the consequence of the disorder in the vicinity of magnetic transitions [18]. The nature of these phase transitions is largely unknown. Manganites are highly correlated systems in which several interactions (electron-

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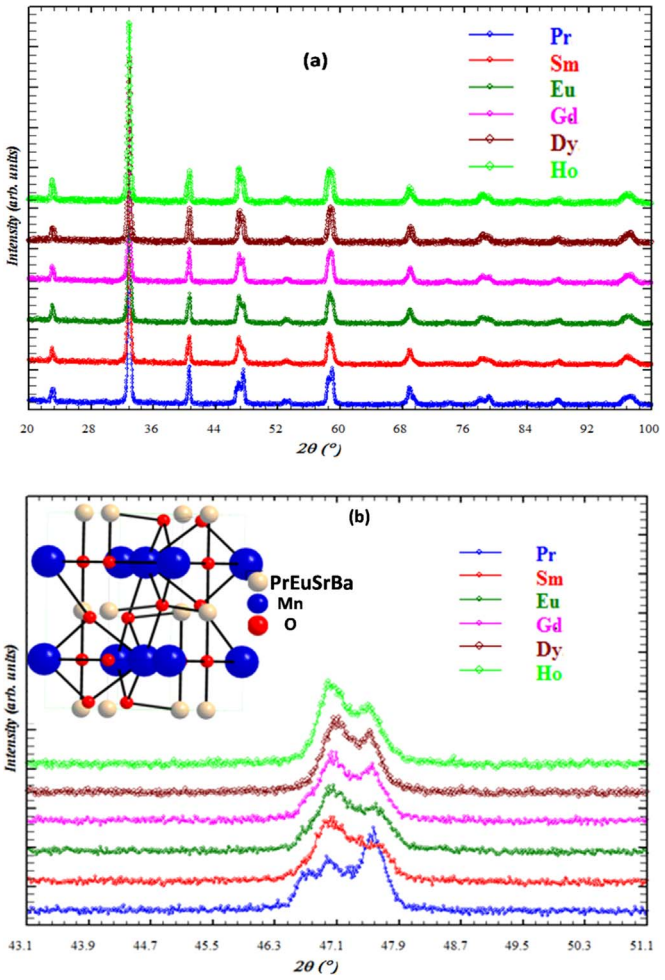

Fig. 1. (a) X-ray diffraction patterns of $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ (Re = Pr, Sm, Eu Gd, Dy and Ho) samples. (b) The zoom on XRD peaks around 2θ = 47° for all the samples.

electron, electron-phonon…) compete in an extremely tight manner. The low energy separating the electronic phases in manganites has led to a description of their properties according to PS phenomenon. It should be understood here that the PS in these compound can take place in the case where the stoichiometry varies from one region to another. Such phenomenon explains also how a magnetic field can transform an insulating phase into a metallic one by percolating the second through the first under the influence of external parameters, especially the disorder. Indeed, a small disorder is sufficient to generate the PS in some manganites.

In this context, the nature of PS and the effect of quenched disorder in $Pr_{0.5}Sr_{0.5}MnO_3$ has been studied by several authors. This compound

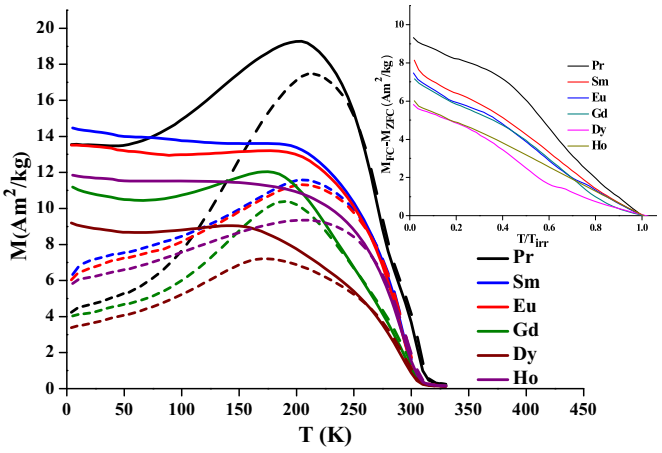

Fig. 2. Temperature dependence of FC (solid line) and ZFC (dashed line) magnetization for the $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ (Re = Pr, Sm, Eu Gd, Dy and Ho) samples under a magnetic applied field of 0.05 T. The inset shows temperature dependence of M_{FC} - M_{ZFC} as a function of T/T_{irr}.

Table 2
The irreversibility temperature, the blocking temperature, the saturation magnetization at 5 K under 7 T, the spontaneous magnetization at 5 K and the volume fraction of FM domains estimated from the spontaneous magnetization for the $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ (Re = Pr, Sm, Eu, Gd, Dy and Ho) samples.

Samples	Pr	Sm	Eu	Gd	Dy	Ho
T_{irr}	255	265	265	250	260	265
T_B	210	205	205	190	175	205
T_{irr}-T_B	45	60	60	60	85	60
$M_{satur}(\mu_B/Mn)$	2.25	2.12	2.10	2.60	2.08	2.19
M_{Spont} (μ_B/Mn)	1.54	1.81	1.76	1.86	1.46	1.71
V_{FM} (%)	44.10	51.71	50.28	53.14	41.60	48.85

crystallizes in tetragonal structure with *I4/mcm* space group and it exhibits two distinct magnetic transitions with decreasing temperature: a paramagnetic (PM)-FM transition at T_C = 265 K and a FM-AFM transition at T_N = 150 K [19–23].

In this work, we have tried to study the mismatch effect σ^2 on the structural and magnetic properties of $Pr_{0.5}Sr_{0.5}MnO_3$. For this, we have prepared several samples $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ (Re = Pr, Sm, Eu, Gd, Dy and Ho). Ba content was chosen in order to keep all the samples with the same average ionic radius at A site of the $Pr_{0.5}Sr_{0.5}MnO_3$ compound ($< r_A >$ = 1.2445 Å). Such study will allow the investigation of the mismatch effect on the magnetic phase coexistence (FM and AFM domains) inside the structure as well as the transition temperatures dependence (T_C and T_N) of structural disorder.

Table 1
Structural parameters and mismatch size for the $Pr_{0.4}Re_{0.1}Sr_{0.5-y}Ba_yMnO_3$ (Re = Pr, Sm, Eu, Gd, Dy and Ho) samples.

Samples	**Pr**	**Sm**	**Eu**	**Gd**	**Dy**	**Ho**
y (Ba content)	0.000	0.030	0.037	0.045	0.060	0.067
a(Å)	5.405(13)	5.445(8)	5.442(7)	5.450(8)	5.429(6)	5.419(9)
b(Å)	5.405(13)	5.406(10)	5.406(7)	5.475(9)	5.440(7)	5.437(11)
c(Å)	7.746(9)	7.747(11)	7.747(6)	7.647(9)	7.748(8)	7.743(10)
V(Å³)	226.31	228.033	228.07	228.21	228.81	228.14
< Mn-O_1 > (Å)	1.978(8)	1.938(2)	1.94(7)	1.943(6)	1.965(11)	1.941(4)
< Mn-O_{21} > (Å)	1.72(3)	1.68(3)	1.74(3)	1.86(5)	1.93(5)	2.11(3)
< Mn-O_{22} > (Å)	2.12(3)	2.21(2)	2.18(2)	2.03(5)	1.96(5)	1.78(4)
< Mn-O_1-Mn > (deg.)	156.6(3)	176.5(10)	179.0(4)	159.5(3)	159.8(4)	171.6(17)
< Mn-O_2-Mn > (deg.)	170.3(12)	160.1(11)	156.7(10)	166.0(2)	161.0(2)	161.2(15)
σ^2 (10^{-3} Å²)	4.29	6.77	7.18	7.87	9.26	10.01
χ^2	1.85	1.74	1.71	1.40	1.60	1.62