

Effects of substitution of some rare earth on the structural and magnetic properties in the site (A) of $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$, where Ln=Nd and Sm compound.

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Abstract

The present study reports the effect of rare earth doping on the structural and magnetic properties in the $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$, where Ln=Nd and Sm Ruddlesden Popper-type. The studied specimens were synthesized as powder samples by solid state reaction at high temperature. The analysis by powder X-ray diffraction using Rietveld refinement showed the crystallization in the tetragonal system for all compounds. The magnetic measurements were studied as a function of temperature ($T = 2-300$ K). When the temperature decreases, each compound has shown first a ferromagnetic-paramagnetic (FM-PM) transition and then an antiferromagnetic-ferromagnetic (AFM-FM) one. The transition temperatures are found to be rare earth doping dependent. For all compounds, a spin-glass phenomenon is evidenced by FC/ZFC magnetization curves.

Keywords: Ruddlesden-Popper, structural, magnetic and spin-glass phenomenon;

1. Introduction

Besides the perovskite family, the Ruddlesden-Popper manganites, which consist of a regular intergrowth of single rock-salt with multiple perovskite layers, were studied most extensively. The crystal chemistry of these oxides shows numerous studies, which are complex and subject to controversy [1]. The $\text{Ca}_2\text{LnMnO}_4$ compounds (Ln=Pr, Sm, Gd, Ho...) are good examples of Ruddlesden-Popper manganites. These compounds display diverse magnetic and electronic phases such as antiferromagnetic (AFM) insulating, ferromagnetic (FM) conductor, paramagnetic (PM) insulating [2], spin-glass [3-5] and charge-ordering [6]. In the other hand, these Ruddlesden-Popper manganites display interest magnetic properties depending on materials-doping, multiple phase transitions, saturation and no-saturation magnetization. The Ln-doped manganites of Ca_2MnO_4 compound induces a mixed valence state ($\text{Mn}^{3+}/\text{Mn}^{4+}$) and enhances magnetic behavior transition; which can be explained by the double exchange interaction between Mn^{3+} and Mn^{4+} ions [7]. It has been shown that $\text{Ca}_2\text{LnMnO}_4$ (Ln=Pr, Sm, Gd, Ho...) compounds, which despite their pure bidimensional character submit a spin-glass transition at low temperatures. For the praseodymium phases $\text{Ca}_2\text{PrMnO}_4$, all compounds exhibit semiconductor behavior. In this paper, we report the effect of Nd and Sm doping on structure and magnetic properties of $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ compounds.

2. Experimental section

Specimens of $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ (Ln=Nd, Sm) were prepared by solid state reaction method [8]. The CaO , Ln_2O_3 and MnO_2 precursors (all of 99.9% purity) were mixed in appropriate ratios. The obtained powders were pressed under 4 tones into pellets about 1 mm thickness and 8 mm diameter and sintered at 1373 K for 4 days in air with several intermediate regrinding and repressing into pellets. Finally, the mixtures were calcined in air at 1523 K for 24 h on Pt boat. The microstructure was observed by scanning electron microscope (SEM). The pictures were taken at room temperature on a Philips XL 30 equipped with a field emission gun at 19.7 kV. The structure was characterized at room temperature by X-ray powder diffractometer (Siemens D5000) with $\text{Cu-K}\alpha$ radiations ($\lambda = 1.54056 \text{ \AA}$). The phase analysis was checked using FULLPROF program based on the Rietveld method. The magnetization measurements were carried out using a vibrating sample magnetometer in the temperature range 2-300K under an applied field up to 0.07 T.

3. Results and discussion

3.1. Structural properties:

In order to make sure that all samples are single phase and all chemical elements (Ca, Ln, Mn, and O) are present in $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ compounds, XRD and EDAX analysis have been realized. Using Fullprof

program, the diffraction peaks corresponding to $x=0.000$ (Fig. 1) can be indexed in the tetragonal system with

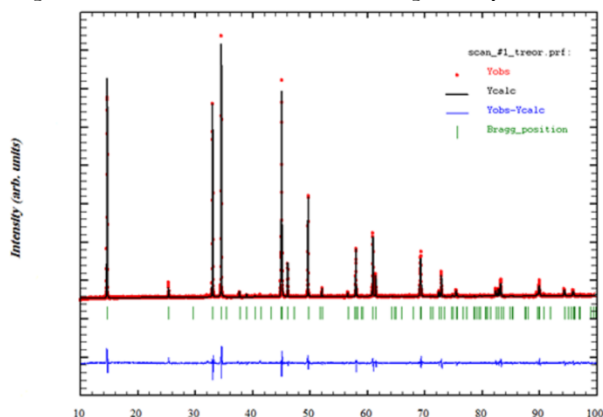


Figure 1. Observed (dots) and calculated Rietveld refinement plots of the XRD parent compound Ca_2MnO_4 . The difference between observed and calculated is shown at the bottom. Vertical tick marks represent Bragg positions.

Table 1: Space group and Rietveld refinement parameters results of $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ compounds.

	Space group	a (Å)	b (Å)	c (Å)
Ca_2MnO_4	I 41/acd	5.183	5.183	24.117
$\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$	I 4/mmm	3.728	3.728	11.93
$\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$	I 4/mmm	3.729	3.729	11.93

3.2. Magnetic properties:

A systematic investigation of magnetization with temperature has been undertaken at an applied magnetic field of 0.07 T for all samples (Fig. 3). When increasing temperature, all specimens show a ferromagnetic-paramagnetic transition (FM-PM) one, at Curie temperature (T_c). The substitution of Ca by Sm leads to the appearance of a second transition at a temperature known as the Neel temperature noted TN. However, this transition does not appear in the case of doping with Nd and the undoped case. This is explained by the fact that the samarium is an element antiferromagnetic (Fig. 4). These two transitions occur at the Curie temperature (T_c) and the Neel temperature (T_N) determined from the pick of $(-dM/dT)$ vs. T curves (Fig. 4). For all compounds, the Curie temperature T_c was found to be constant (around 105 K) and independent to the applied field.

In the other hand, the substitution provides the Mn^{3+} ions and induces a mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence, enhancing the

$I41/acd$ space group. This result is in agreement with those found by Takahashi et al. [9] and Fawcett et al. [10].

The substitution of Ca by Nd or Sm generates spectral modifications a little different to Fig. 1, and the diffraction peaks can be indexed in the same tetragonal system with $I4/mmm$ space group [11]. The lattice constants of $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ at room temperature are given in Table 1.

Fig. 2 shows an example of EDAX analysis spectral realized at room temperature for Ca_2MnO_4 , $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$ and $\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$ compounds ($x=0.200$). This analysis reveals that all elements are present and any element has been volatilized in the course of the heating for all x compositions.

conduction by e_s electrons hopping through $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ system [12, 13]. Such physical phenomenon, called double exchange (DE), is proved by Zener [14] and used by several authors to explain the electrical transport and the magnetic properties undoped manganites. This DE, characterized by a FM state, explains the increase of magnetization with the doped rare earths. These values of magnetization are given in Fig. 5. So, the Sm-doping leads to a competition between two states, AFM and FM, during the doping. This behavior, related to the presence of ferromagnetic nano-domains coupled together by complex interactions (FM and AFM), promotes the formation of a spin glass [15]. To verify the existence of such system, measurements of magnetization in ZFC and FC mode was performed (Fig. 6). It should be noticed that, for all samples, the ZFC curve does not coincide with FC curve below a given temperature T_{sg} , which is a characteristic of a spin-glass order [11]. These values are given in Table 2.

Table 2: values of Weiss temperature, experimental effective paramagnetic moments and spin-glass temperature of $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ compounds.

Echantillons	θ_p (K)	μ_{eff}^{exp} (μ_B)	T_{SG} (K)
Ca_2MnO_4	100	3.887	101
$\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$	104	3.62	101
$\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$	99.88	3.91	53

From this table, we can deduce that the temperature spin glass for $\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$ made is very low comparing to $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$. This difference is mainly due to an AFM behavior of Sm. **Fig. 7** shows the temperature dependence of inverse magnetic susceptibility χ^{-1} at different magnetic field. As is well known for FM system, the relation between χ and the temperature T should follow the Curie-Weiss law in the PM region:

$$\chi = \frac{C}{T - \theta_p}$$

where C and θ_p are the Curie constant and the Weiss temperature, respectively. C and θ_p were obtained by fitting the linear paramagnetic region of $\chi(T)$ curve. The experimental effective paramagnetic moments were calculated from the following formula:

$$C = \frac{N_A \mu_B^2}{3k_B} \mu_{\text{eff}}^2$$

where $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ is the number of Avogadro, $\mu_B = 9.274 \times 10^{-21} \text{ emu}$ is the Bohr magneton and $k_B = 1.38016 \times 10^{-23} \text{ J.K}^{-1}$ is the Boltzmann constant. θ_p and μ_{eff} are listed in **Table 2**, where it can be seen that the substitution of Ca ion by Sm and Nd one leads to the lightweight decrease of the Weiss temperature. The positive θ_p values indicate a FM interaction between spins. Moreover, the decrease of effective magnetic moment from the $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$ is related to the AFM behavior, due of Sm element inserted. In addition, the FM to behavior is related to the substitution of Ca ion by Nd ones, which increases the effective magnetic moment of the $\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$.

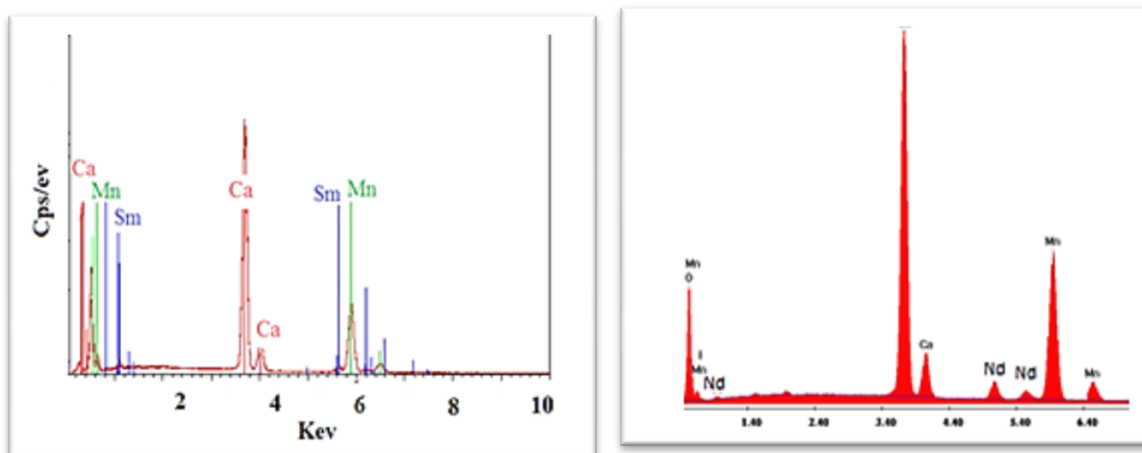


Figure 2. EDAX analysis of $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$ and $\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$ compounds

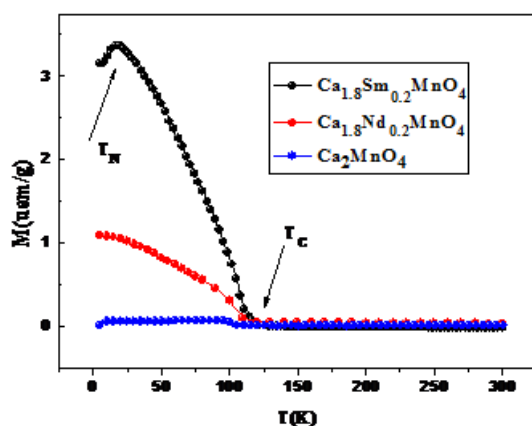


Figure 3. Temperature dependence of magnetization measured at 0.07 T for Ca_2MnO_4 , $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$ and $\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$ compounds

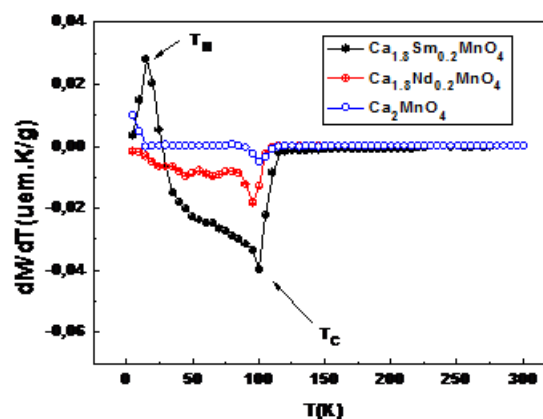


Figure 4. Variation of (dM/dT) as function of temperature T for all compounds at an applied magnetic field of 0.07 T.

4. Conclusion

In this work, we have investigated the structure and magnetic properties of Ruddlesden Popper family Ca_2MnO_4 , $\text{Ca}_{1.8}\text{Nd}_{0.2}\text{MnO}_4$ and $\text{Ca}_{1.8}\text{Sm}_{0.2}\text{MnO}_4$ compounds. There is no structural transition due to substitution of Ca^{2+} by Ln^{3+} . All the samples crystallize in a tetragonal structure: with space group $I41/acd$ for $x = 0$ and $I4/mmm$ for $\text{Ca}_{1.8}\text{Ln}_{0.2}\text{MnO}_4$. The Curie temperature

TC is found to be around 105 K for all samples. At low temperature, the Nd, Sm-doping leads to a competition between the AFM and FM states, and promotes the formation of a spin-glass state. This state is confirmed by a magnetization study in ZFC and FC mode. This last phenomena is absent for Nd dopage, and as for the undoped compound.

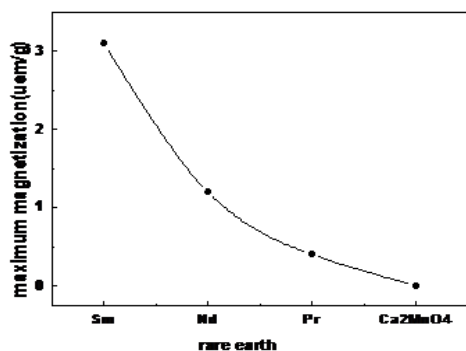


Figure 5. variation of the magnetization as a function of substituted rare earth.

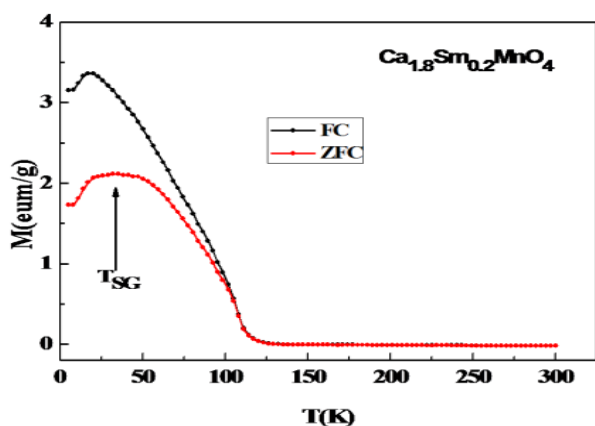
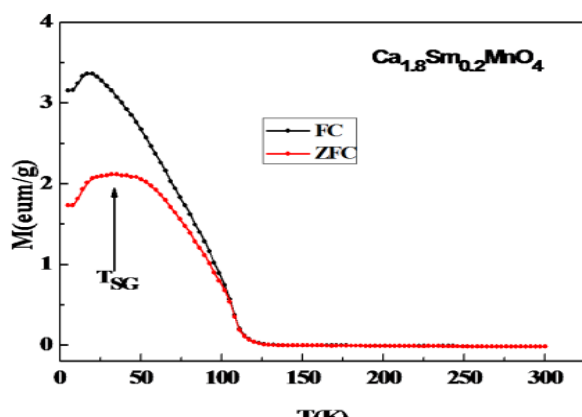
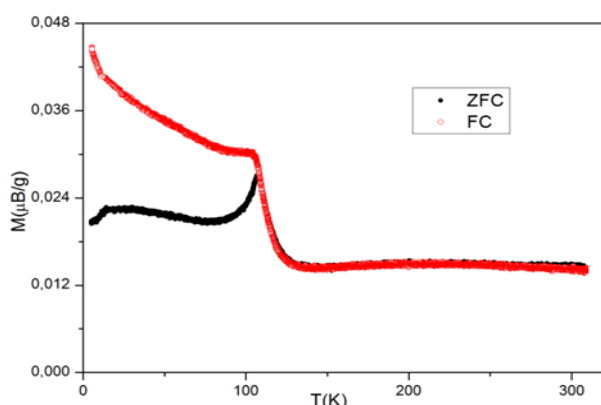


Figure 6. Magnetization (M) as a function of temperature (T) for all compounds measured at 0.07 T under the field-cooled (FC) and zero-field-cooled (ZFC) modes

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