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Structural and magnetic properties of Al doped $Y_2CaMn_3O_9$ perovskites

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The $Y_2CaMn_{3-x}Al_xO_9$ perovskites crystallize in an orthorhombic type structure having Pnma-space group. The magnetic measurements show the presence of spin-glass type behavior. The maxima in the temperature dependences of the magnetization in ZFC sample, decrease from T_m= 30 K (x=0) to 18.9 K (x=0.6). The magnetization isotherms in field up to 90 kOe show that the saturation is not obtained. Above T_{SRF} temperature, Curie-Weiss type behavior was evidenced. The number of Mn^{4+} ions increases as Mn is substituted by Al. In the temperature range $T_c < T < T_{SRF}$ ferromagnetically ordered clusters are coupled by random dipolar interactions.

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1. Introduction

$CaMnO_3$ crystallizes in an orthorhombic type structure having Pnma space group [1]. The Mn^{4+} ion has an octahedral oxygen coordination with an axial oxygen (O1) and two equatorial ones (O2 and O22). Ca^{2+} occupies the center of a distorted dodecahedron of oxygens. $YMnO_3$ crystallizes in a hexagonal structure having $P6_3cm$ space group. The two independent Y^{3+} ions are coordinated by seven oxygens, while the Mn^{3+} is pentacoordinated by oxygen atoms [2]. The crystal structure of $Y_xCa_{1-x}MnO_3$ system has been extensively studied [3-6]. According to Vega et al. [6] orthorhombic phases were detected in the range $0.0 \leq x \leq 0.25$ (O – phase). In this region, Ca site is twelvefold coordinated. Orthorhombic O' type phases were evidenced in the region $0.50 \leq x \leq 0.75$ where Ca site is ninefold coordinated. In the composition range $0.25 \leq x \leq 0.50$, the coexistence of both O and O' type structures was shown. $YMnO_3$ segregates as a separate phase for x>0.75. According to Vega et al. [6] the oxygen content in manganite perovskites having O' type structure remains unchanged, at δ=3.00.

The $CaMnO_3$ presents a G-type antiferromagnetic (AF) ordering with a transition temperature T_N= 123 K, and an insulator behavior. The manganese ions have valence 4+, where the localized t_{2g} spins have S=3/2. As yttrium ions replace calcium ones, itinerant e_g electrons with spins S = 1/2 are introduced and there is a mixed valence system having both Mn^{3+} and Mn^{4+} ions. When increasing Mn^{3+} content, the antiferromagnetic state is suppressed and an essentially ferromagnetic state appears for 0.2<x<0.5 [7]. The magnetic behavior can be described by the electron hopping via double exchange (DE) interactions between Mn^{3+} and Mn^{4+}. The spins of the charge carriers (e_g electrons or holes) are aligned parallel to the local spin (t_{2g}) by Hund rule and hop from one ion to next, without changing their spin orientation. This results in an effective ferromagnetic interaction. Generally, there is a competition between ferromagnetic and antiferromagnetic interactions in mixed valence manganese perovskites. For x>0.5, the antiferromagnetic superexchange interactions dominate over the double exchange ferromagnetic ones. A spin-glass or mictomagnetic behavior is present. The average ionic radius of A (A=Ca, Y) site, $<r_A>$, is an important parameter that determines the magnetic proprieties in $La_xCa_{1-x}MnO_3$ perovskites. When decreasing $<r_A>$ the Curie temperatures, T_c diminishes [8].

In this paper we analyze the crystal structures and magnetic proprieties of $Y_2CaMn_{3-x}Al_xO_9$ perovskites, where the end series compound (x=0) crystallizes in an orthorhombic O'-type structure.

2. Experimental set-up

The $Y_2CaMn_{3-x}Al_xO_9$ perovskites with x=0, 0.3 and 0.6 were prepared by standard ceramic procedure. Stoichiometric proportions of Y_2O_3, $CaCO_3$, $MnCO_3$ and Al_2O_3, having analytical purities, were grounded and mixed together and pre-sintered at 1250 °C for 48 hrs. After that, pellets were prepared and finally sintered at 1425 °C, in air, for 12 hrs.

Powder X-ray diffraction patterns were taken at ambient temperature by using a Brucker D8 diffractometer with Cu target and graphite monochromatizor. Rietveld refinements were performed by using the Topas code.

The temperature dependences of the magnetizations of the zero field-cooled (ZFC) and field cooled (FC) samples were studied in the temperature range 4.2 - 100 K using an Oxford Instruments type equipment. The magnetic isotherms were obtained in fields up to 90 kOe. The magnetic susceptibilities, in the paramagnetic range, were determined with a Faraday type balance in a field of 10 kOe.

3. Experimental results

The $Y_2CaMn_{3-x}Al_xO_9$ perovskites having x≤ 0.6 crystallize in an orthorhombic type structure having Pnma space group. When increasing the aluminum content, the cell volumes decrease by 0.13 % (x=0.3) and 0.29 % (x=0.6) as compared to the parent compound. This behavior can be correlated with smaller Al^{3+} radius as referred to either Mn^{3+} or Mn^{4+} one. There is a compressive strain in the lattice, causing a decrease mainly in the “a” lattice parameters (Fig. 1). Since the Y^{3+} radius is smaller than of Ca^{2+} one, the average radius of the A site, $\langle r_A\rangle \cong 1.18$ Å in $Y_2CaMn_3O_9$ perovskite is smaller than $\langle r_{Ca}\rangle$ in $CaMnO_3$. Since $\langle r_A\rangle$ controls the bond angles, values of Mn-O1-Mn and Mn-O2-Mn angles for $Y_2CaMn_3O_9$ of $145.7(4)^0$ and $148.1(5)^0$, respectively were shown. A small increase of bond angles can be seen when Mn is replaced by Al. Thus, for $Y_2CaMn_{2.4}Al_{0.6}O_9$, values $147.9(2)^0$ and $150.1(3)^0$, respectively were determined. This behavior may be correlated with the lattice distortions as result of aluminum substitution. The tolerance factor $t=R_A+R_O/\sqrt{2}(R_M+R_O)$ and steric factor $s=\langle A\text{-}O\rangle/\sqrt{2}\langle Mn\text{-}O\rangle$ are $t \cong s \cong 0.89$. This low tolerance factor can be associated with high rotation and tilting angles (Fig. 2). We note that a similar result was reported in case of $Y_{0.7}Ca_{0.3}MnO_3$ perovskite [6]. The tilt and rotation angles decrease as the manganese is gradually replaced by aluminum (Fig. 2).

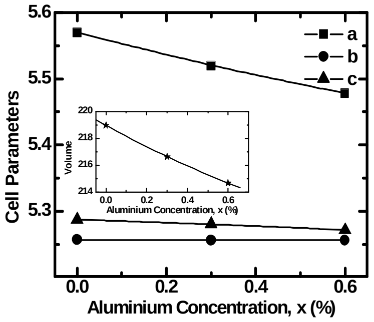


Fig. 1. Composition dependences of lattice parameters and volumes.

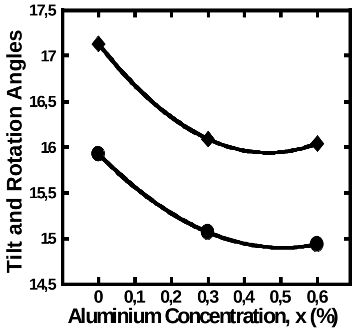


Fig. 2. Tilt (◊) and rotation (○) angles of the MnO_6 octahedron.

The magnetization isotherms, at 4.2 K, are plotted in Fig. 3. The magnetizations increase gradually as the external field increases, but no saturation can be obtained. The isotherms are typical for a spin-glass or mictomagnetic behavior. The magnetizations are smaller as a higher number of manganese atoms are substituted by aluminum. To obtain additional data on the magnetic behavior of the above system we analyzed the temperature dependences of the magnetizations, in low field, both for zero field cooled (ZFC) and field cooled (FC) samples – Fig. 4. These also support the presence of spin-glass (or mictomagnetic) type behavior. A high irreversibility in ZFC and FC magnetizations occur for T≤60 K. There are maxima in temperature dependences of magnetizations in ZFC samples. The temperatures, wher maxima appear, decrease from T_m = 30 K (x=0) to 18.9 K (x=0.6). From χ vs. T curves, Curie temperatures T_c=50 K (x=0), 48 K (x=0.3) and 46 K (x=0.6) are suggested.

The temperature dependences of the magnetic susceptibilities in the paramagnetic range, follow a Curie–Weiss law: $\chi=C(T-\theta)^{-1}$ (Fig. 5). We denoted by C the Curie constant and θ is the paramagnetic Curie temperature. The C and θ values obtained by fitting the experimental data are listed in Table 1. The θ values increase from 83.7 K (x=0) to 98 K (x=0.6). Assuming that the effective moments of $Mn^{3+}$and Mn^{4+} are given by the free ion values, we determined their composition dependence – Table 1. When manganese is gradually substituted by aluminum, the number of Mn^{4+} ions increase. This variation can be correlated with the occurrence of oxygen vacancies within lattice and/or the presence of Al^{3+} ions, which replaces Mn^{3+} ones. Since aluminum has a fixed valence state (3+) the latter mechanism seems to be dominant.

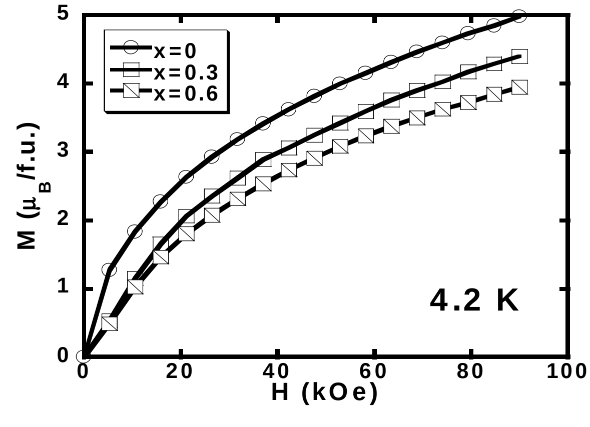
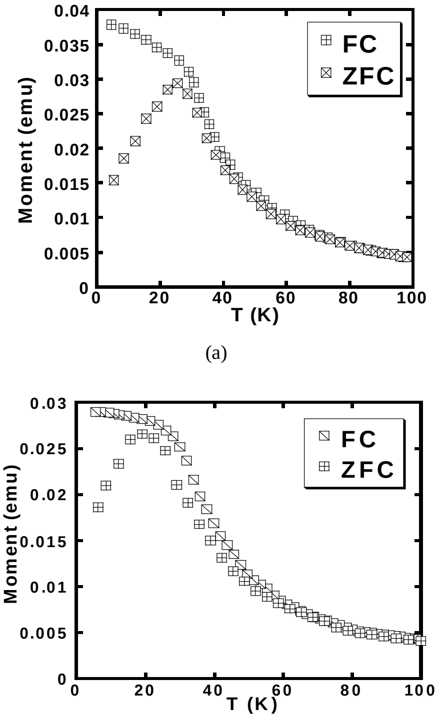


Fig. 3. The magnetization isotherms for $Y_2CaMn_{3-x}Al_xO_9$ perovskites at 4.2 K.



(a)

(b)

Fig. 4. The FC and ZFC magnetizations for $Y_2CaMn_{3-x}Al_xO_9$ with $x=0.3$ (a) and 0.6 (b) in field of 500 Oe.

Table 1. Magnetic properties of $Y_2CaMn_{3-x}Al_xO_9$ perovskites.

	x=0	x=0.3	x=0.6
Curie constant (K*emu/mol)	7.82	7.00	6.08
Θ (K)	83.7	84.3	98.7
Mn^{4+} (%)	33.6	34.4	39.5
Mn^{3+} (%)	66.4	65.6	60.5
T_m (K)	30	25.5	18.9

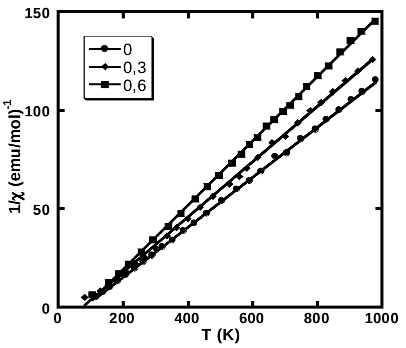


Fig. 5. The temperature dependence of the reciprocal susceptibilities for $Y_2CaMn_{3-x}Al_xO_9$ perovskites.

4. Discussion and conclusions

The decrease of the T_m and T_c values when increasing the aluminum content may be correlated mainly with dilution effect. The exchange interactions of the Mn^{3+}-O-Mn^{4+} type are partially broken as result of the Al substitutions. In this case there are also Al^{3+}-O-Mn^{4+} connections. The slight increase of bond angles may contribute only little to the increase of T_c values but these are strongly compensated by the above dilution effects.

As mentioned already, a Curie-Weiss behavior was observed only at temperatures above T_{SRF}, rather high. For $T_c<T<T_{SRF}$ there is a deviation from a Curie-Weiss law, suggesting the presence of magnetic correlations related to ferromagnetically ordered clusters and the random dipolar interactions between their moments. Short-range magnetic correlations above T_c were already evidenced by small angle scattering experiments [9] or by magnetic measurements [10,11]. This can explain the non-equilibrium dynamics observed at $T>T_m$ in $Y_{0.7}Ca_{0.3}MnO_3$ perovskite [12]. An inhomogeneous distribution of Al^{3+} ions in matrix, i.e. of Mn^{4+} ions could induce the formation of $Mn^{4+}$and Mn^{3+} rich clusters. This fact can increase the temperature range in which ferromagnetic cluster are present. In this way the increase of the paramagnetic Curie temperatures, when increasing aluminum content can be explained.

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