STRUCTURE AND PROPERTIES OF DOUBLE PEROVSKITE SYSTEM $La_2Co_{1-x}Fe_xMnO_6$

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Abstract. *Low Fe-doped insulating ferromagnets La_2CoMnO_6 were prepared and studied. The compounds crystallized in orthorhombic space group Pnma with slight changes in the lattice constants. We have observed a significant reduction of resistivity due to doping, together with an increase of magnetization and saturated magnetization as doping level increased. The doping also reduced T_C for both transitions at around 220 and 140 K which attribute for the different spin orderings of the magnetic ions. The small features were also seen at around 40 K and should correspond to the cluster glassy region with spin disorders.*

Keywords: Structure, Magnetism, Fe-doped, La_2CoMnO_6.

I. INTRODUCTION

The ferroelectric insulators of a form RE_2AMnO_6 where RE is a rear earth element and A a transition metal attract a lot of interests due to a co-existence of ferromagnetism and insulating state within a single structural frame [1,2]. Among the effects that were found in these double perovksites is the dependence of dielectric permitivity on magnetic field which promises direct application in spintronics as the magnetic field driven capacitors. The double perovskites inherits from the single ones a structural type that is built up from the connecting MnO_6 polyhedrons, but here the polyhedrons are connected only in (x,y) plane and in the (z) direction one inserted AO_2 layer intercepts the continuity of MnO_6 network. For a particular case of La_2CoMnO_6 (RE = La, A = Co) there are clearly two sub-lattices of MnO_6 and CoO_6 which are alternating each other along z direction but are competing in (x, y) plane. Therefore, besides a ferromagnetic component that arises from a double exchange (DE) interactions between manganese ions (Mn^{3+}- O

Mn^{4+}), there are also components arisen from exchange interactions between cobaltate ions themselves and between cobaltate and manganese ions. The ordering of magnetic ions within a lattice of RE_2AMnO_6 is influenced by various factors (preparation routes, thermal treatment conditions such as time, gradient, ramping, cooling etc) and certainly determines the integral magnetic properties of compound. Thus it is not a surprise that La_2CoMnO_6 shows two major ferromagnetic transitions with Curie temperatures T_C at around 220 and 140 K, together with a minor transition at a lower temperature around 40 K [3–5]. While the first two transitions results caused by the ordering states of the high spin $Co^{2+}\left(t_{2g}^3 e_g^2\right)$ and $Mn^{4+}\left(t_{2g}^3 e_g^0\right)$ ions ($T_C \sim 220$ K), and of the intermediate spin $Co^{3+}\left(t_{2g}^3 e_g^2\right)$ and high spin $Mn^{3+}\left(t_{2g}^3 e_g^1\right)$ ions ($T_C \sim 140$ K), the nature of the third transition ($T_C \sim 40$ K) is not quite clear, although the evidences exist to demonstrate a reentrant glass behavior at low temperature [5, 6]. The available literatures point to a mere correspondence between the sintering temperature and T_C: samples sintered at lower temperature tend to show higher T_C whereas the ones sintered at higher temperature usually exhibit lower T_C [5, 6]. The reentrant glass behavior has been demonstrated for $Sr_2Fe_{1-x}Mn_xMoO_6$ [7] in which the appearance of a random spin ordering was attributed to the competition between the nearest neighbor clusters. This competition was caused by the substitution of Fe which introduced the super-exchange (SE) antiferromagnetic pairs Fe^{3+} - O Mn^{3+}. While the magnetic phase transitions in La_2CoMnO_6 appear complicated, the compound did not show any abrupt changes in its conduction mode, which may be expressed, with addequate experimental accuracy, as of variable range hopping (VRH) mode with thermal activation energy of order 150 - 180 meV [6]. Although the bulk compound La_2CoMnO_6 has been carefully studied, its doped compounds, especially the ones with Fe, still leave many questions that need to be clarified. First and foremost is a role of Fe and its effect on T_C in a multiferroic with different transition temperatures. As known for single perovskites [8] the doping of Fe showed a monotoneous effect on magnetic properties only at low concentration where the charge disproportionation (CD) phenomenon did not occur, that is, when two Fe substitution sites were distanced from each other and the unpaired electrons of two Fe4+ ions were not disproportionately located so that $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ [9]. The occurence of the multi-spin low valent Fe^{2+} and high valent Fe^{5+} ions at higher doping concentration usually complicate the final image of magnetic interactions, so we restricted our case to the doping of Fe upto a concentration of 3%.
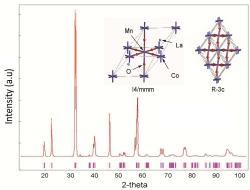
II. EXPERIMENTAL

The $La_2Co_{1-x}Fe_xMnO_6$ (LCFM) bulk samples were prepared by traditional solid-state reaction method with highly purified $CaCO_3$, MnO_2, La_2O_3 and Fe_2O_3 (Merck, $> 99.9\%$) powders as the precursors. The parent oxides were dried, then weighted to the required molar proportions and mixed together and ground for 4 hours. The mixture was ground again for the next 4 hours in ethanol then pressed into the pellets (5 tons/cm^2, no bonding colloid was applied) of height 2 mm and diameter 10 mm. The pellets were sintered at 700˚C for 4 hours. The sintered pellets were ground again for 4h and pressed, then calcinated at 1250˚C for one week in open air and at constant ramping rate 2˚C/min. The structure characterization was taken on a Bruker's D5005 diffractometer equipped with CuK_α radiation source ($\lambda = 1.54018$Å) and a monochromator of slit size 0.5 mm. The step width was 0.02˚. The resistivity measurement was performed by using the standard 4-probe technique with straight alignment of electrodes on a Bio-Rad Deep

Level Transient Spectroscopy system. The magnetic measurement was taken on from 2 K to room temperature on a Physical Property Measurement System (PPMS) from Quantum Design.

III. RESULTS AND DISCUSSION

Similar to the cases of many single perovskites, our doped and undoped La$_2$CoMnO$_6$ preferrably crystallized in an orthorhombic space group Pnma (No.62) which is a lower symmetry than of the ideal face-center cubic lattice of perovskites. The lattice constants derived from Rietveld analysis of profiles are listed in Table 1 and the sample diffractogram for the undoped La$_2$CoMnO$_6$ is featured in Fig. 1. Commonly, RE$_2$AMnO$_6$ may also be found in a tetragonal space group $I4/mmm$ of higher symmetry than *Pnma* (which can be obtained from the orthorhombic symmetry by acquiring $a = b$) and in a monoclinic space group $P2_1/n$ of lower symmetry ($\beta \neq 90°$) [1]. From the orthorhombic lattice a reduced cell with $Z = 2$ may be deduced as given in Ref. [2], i.e. space group $R\overline{3}$, $a = b = c = 5.488$Å, $\alpha = \beta = \gamma = 60.72°$. This reduced cell contains exactly two MnO$_6$ layers. For our doped samples, the small doping concentrations did not lead to the visible changes in lattice constants (Table 1). The atomic positions and thermal factors as obtained for the undoped sample from the Rieveld refinement of phases are given in Table 2. The R-factors for weighted profile (R_W) and for integral intensity (R_I) are somehow higher than usual, 22 and 8% respectively, and this situation did not allow us to obtain the refined site occupation factors at Mn and Co sites (in fact, they were fixed at 1.0). Thus, there was a question arose about a correct substitution site of doped Fe atoms. Sto-

Fig. 1. The XRD patterns for the undoped La$_2$CoMnO$_6$. The inset shows the packing coordinations for two different space groups. The doped samples with Fe contents $x \leq 3\%$ show the similar patterns and are omitted for clarity.

Table 1. Cell parameters, curie temperatures, and activation energies for undoped and Fe-doped La$_2$CoMnO$_6$ (s.g. pnma, no.62)

x	Cell constants [Å]			T_C [K]	E_g [meV]
	a	b	c		
0.00	5.525	5.476	7.773	215	155
0.01	5.525	5.482	7.775	175	122
0.02	5.524	5.479	7.778	153	79
0.03	5.526	5.471	7.777	130	54

Table 2. Atomic positions and isotropic thermal motion factor (BISO) for the undoped La$_2$CoMnO$_6$ (s.g. pnma, no.62). $R_W = 22\%$, $R_I = 8\%$.
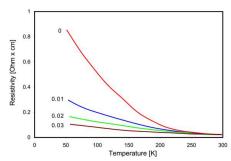
Atom	x	y	z	BISO
La	0.52	1/2	1/4	0.71
Co	0	0	0	0.82
Mn	1/2	1/2	0	0.56
O1	0	0	1/4	1.21
O2	0.27	0.022	0.714	1.10

ichimetrically given, Fe should be substituted for Co, but as the Co and Mn sites were crystallographically equivalent, the Fe atoms might substitute for both Co and Mn. Unfortunately, the accuracy achieved with X-ray diffraction measurements in our case did not allow to clarify this situation crystallographically.
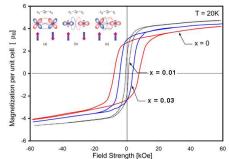
The substitution of Fe strongly affected the resistivities of samples as seen in Fig. 2. The doping reduced the resistivity by orders of magnitude but in overall our samples showed the higher resistivities in comparison with that of other works [10,11,12]. As observed, the resistivities decreased upon doping with the decreasing tendency as temperature lowers (unitl 50 K). However, there was no abrupt change in the $\rho(T)$ curves which might signify some phase transition. We fitted the $\rho(T)$ curves according to VRH model and list the obtained activation energies given in Table 1. These values are comparable to the ones obtained by the other authors [10–12].

The magnetization versus field measured at 20 K is given in Fig. 3. The inset in Fig. 3 illustrates the possible spin exchanges mediated through oxygen $2p$ orbitals between t_{2g} and e_g electrons of the metals according to Ref. [1] (Kanamori-Goodenough rule). The FM state which prevails below the Curie temperature is a result of a half-fill $M(t_{2g}) - O(2p) - M(e_g)$ interaction. The other possible pairs such as $M(t_{2g}) - O(p\pi) - M(t_{2g})$ and $M(e_g) - O(p\sigma) - M(e_g)$ are all antiferromagnetic. As seen in Fig. 3, the Fe-doping increased both magnetization and saturated magnetization while lowered the T_C accordingly (Table 1). The doping also reduced coercive forces H_C but this effect could only be seen at low temoperature. Above the Curie temperature T_C all magnetization curves yield $H_C \approx 0$. Besides, the magnetization decreased as temperature increased and at room temperature the magnetization was about 20% as of that at 5 K. We have obtained 4.1 μB per unit cell saturated magnetization on the undoped sample and 5.3 μB on doped one with $x = 0.03$. The values for T_C (Table 1) were determined on basis of fitting the inversed susceptibility χ^{-1} according to the Curie-Weiss law (curve fits not shown).
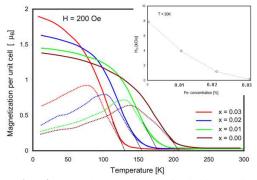
In Fig. 4 we show the dependence of Field Cooling (FC) and Zero-Field Cooling (ZFC) curves on temperature (from which the extrapolation fits for T_C may also be obtained). While

Fig. 2. Dependence of resistivity on temperature from 50 to 300 K.

Fig. 3. Magnetization vs. field at 20 K. The insets show the Kanamori-Goodenough rule according to Ref. [5] and the saturated magnetization obtained at 60 kOe

Fig. 4. The development of Field Cooling (FC) and Zero-Field Cooling (ZFC) magnetization at a constant field of 200 Oe according to temperature from 10 to 300K. The inset shows the evolution of coercive field strength on doping content.

the FC curves showed a continuous increase as temperature decreased, the ZFC curves did separate from the FC curves at the temperatures near T_C and expressed the maxima (seen at 142, 137, 107, 75 K for $x = 0, 0.1, 0.2$ and 0.3, respectively). As discussed, the first transitions with $T_C = 215, 175, 153$ and 130 K (Table 1), are the results of the ordering states of the high spin Co^{2+}($t_{2g}^3 e_g^2$) and Mn^{4+}($t_{2g}^3 e_g^0$) ions, and the second transitions with $T_C = 142, 137, 107, 75$ K are the results of the orderings of the intermediate spin Co^{3+}($t_{2g}^3 e_g^1$) and high spin Mn^{3+}($t_{2g}^3 e_g^1$) ions. There are also the small features near 35 K which may correspond to the transitions observed for the reentrant glassy cluster behavior of doped samples similar to the situation discussed in Ref. [5] for the undoped La$_2$CoMnO$_6$.

IV. CONCLUSION

The small doping of Fe in La$_2$CoMnO$_6$ ($\leq 3\%$) led to the slight changes in the lattice constants but the symmetry of the lattice remained unchanged. The doping led to the observable decreases of the Curie temperatures T_C (from 215 to 130 K for the first and from 142 to 75 K for the second transitions). However the doping also resulted in the enhancement of saturated magnetizations in all samples. The substitution of Fe induced a decrease of resistivity by orders of magnitude but did not alter the conduction mode which was believed to follow the variable range hopping model.

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