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THE STRUCTURAL AND MAGNETIC PROPERTIES OF $La_{1-X}Ca_XMnO_3$ WITH X = 0.27 AND 0.47

Y. E. Gunanto[1], B. Kurniawan[2], S. Poertadji[2], A. A. Wisnu[3],
A. Purwanto[4], H. Tanaka[5] and T. Ono[5]
[1]*Dept. of Math.Educ., Universitas Pelita Harapan,*
Karawaci, Tangerang 15811
[2]*Department of Physics, University of Indonesia,*
Kampus UI, Depok
[3]*Centre of Technology for Nuclear Industrial Materials (PTBIN)-BATAN,*
Kawasan Puspiptek, Serpong 15341, Tangerang Selatan
[4] *Surya Institute, Gading Serpong,*
Tangerang 15811
[5]*Department of Physics, Tokyo Institute of Technology,*
Tokyo, Japan 152-8551
e-mail : yohanes.gunanto@uph.edu

ABSTRACT

THE STRUCTURAL AND MAGNETIC PROPERTIES OF $La_{1-x}Ca_xMnO_3$ WITH x = 0.27 AND 0.47. We have studied the structural and magnetic properties for $La_{1-x}Ca_xMnO_3$ with $x = 0.27$ and 0.47 using neutron powder diffraction and magnetization measurements. At room and low temperature, all samples have the orthorhombic structure with space group *Pnma*. The sample $x = 0.47$ shows the antiferromagnetic mix a ferromagnetic with the magnetic moment and the Curie temperature are 1.30 μ_B and 260 K, respectively while the sample $x = 0.27$ is a ferromagnetic with the magnetic momentand the Curie temperature are 3.10 μ_B and 197 K, respectively.

Keywords: $La_{1-x}Ca_xMnO_3$, Neutron powder diffraction, Magnetization

ABSTRAK

STRUKTUR DAN SIFAT MAGNETIK $La_{1-x}Ca_xMnO_3$ DENGAN x = 0,27 DAN 0,47. Struktural dan sifat magnetik $La_{1-x}Ca_xMnO_3$ dengan x = 0,27 dan 0,47 telah dikaji menggunakan difraksi serbuk neutron dan pengukuran magnetisasi. Pada suhu kamar dan suhu rendah, semua sampel memiliki struktur ortorombik dengan grup ruang *Pnma*. Sampel x = 0,47 menunjukkan campuran antiferromagnetik dan feromagnetik dengan momen magnetik 1,30 μ_B dan suhu *Curie* adalah 260 K, sedangkan sampel x = 0,27 menunjukkan feromagnetik dengan momen magnetik 3,10 μ_B dan suhu *Curie* adalah 197 K.

Kata kunci: $La_{1-x}Ca_xMnO_3$, Neutron difraksi serbuk, Magnetisasi

INTRODUCTION

Perovskite oxide compound with the general formula ABO_3, from rare earth in 3d transition, is one of the important compounds that have been researched in the last decade because of the function in the electronic and magnetic industry. An example of perovskite compound is $LaMnO_3$ or $CaMnO_3$. Partial substitution of the Ca atom towards the La in $LaMnO_3$ creates manganate compound, $La_{1-x}Ca_xMnO_3$ that has Colossal Magnetoresistance (CMR) characteristic. This phenomenon has become interesting topic to know the characteristic of the rare earth manganate that is doped by the other metal [1].

The diagram $La_{1-x}Ca_xMnO_3$ phase shows the differences in the ferromagnetic phase (FM) and anti ferromagnetic (AFM) as the differences in insulator and metal phase [2]. The occurrence of the CMR phenomenon in $La_{1-x}Ca_xMnO_3$ comes from the change of MN^{3+} ion to Mn^{4+} in $LaMnO_3$ as the effect of La-Ca substitution, so the Mn^{3+} and Mn^{4+} mixing valences have to be understood [3]. A minor focus is given to the contribution $CaMnO_3$ fraction in the diagram $La_{1-x}Ca_xMnO_3$ phase (LCMO) [4]. Another thing that has not been known yet is the magnetic condition in the doping regime that has antiferromagnetic reference with the difficulties to differentiate the FM-AFM phase.

So far, the mechanism of the electricity characteristic changes from the semiconductor into conductor and the maximum effect of CMR that get in the T_c curie temperature have not been known yet. The electricity characteristic, *ferromagnetism* and CMR depends on the Mn^{4+} ion that can be created by substituting three valences ions (for example: La) with the two valences ion (for example: Ca) [5]. Thus, we have studied the structural and magnetic properties for $La_{1-x}Ca_xMnO_3$ with x = 0.27 and 0.47 using neutron powder diffraction and magnetization measurements.

EXPERIMENTAL METHOD

The samples were prepared by thoroughly mixing stoichiometric amounts of $CaCO_3$, La_2O_3, MnO_2 and CuO of at least 99.99% purity. The mixed powders were ball milled for 5 hours, heated at 1350 °C for 6 hours, ball milled for 10 hours, heated at 1100 °C for 24 hours and ball milled for 10 minutes. The phase purity was checked by a powder X-Ray Diffraction, which indicated a single phase character of the sample. The neutron powder diffraction experiments were performed with a High Resolution Powder Diffractometer (HRPD) (λ= 1.8223 Å) at the Neutron Scattering Laboratory of BATAN, Serpong, Indonesia. The 4 g sample was loaded in a cylindrical vanadium can and placed in a helium cryostat. The data were collected in the angular range of $2\theta = 2.5\,^{o}$ - $157\,^{o}$ in the interval of $0.05\,^{o}$ for the room temperature measurement and of $0.2\,^{o}$ for the 13 K one. The room temperature measurement was conducted outside the cryostat to allow sample cooling and stabilizing for the low temperature measurement due to limited beam time. The wider interval was due to the limited beam time allocated for the sample.

The data reduction was performed after the measurement. The diffraction patterns were analyzed using the Rietveld reffinement program FULLPROF which can *reûne* the magnetic structure along with the crystallographic structure. The magnetic intensities were also analyzed by extracting integrated intensities for individual peaks and fitted models for the magnetic structures based on symmetry analysis[6,7].

Magnetic susceptibility was measured with a Superconducting Quantum Interference Device (SQUID) magnetometer. The magnetization M-T used the external magnetic field 2 mT.

RESULTS AND DISCUSSION

Crystallographic Structure

The results of XRD diffraction patterns at room temperature indicate that all samples already showed single phase with a crystal structure *orthorhombic* with space group *P nma*. To ensure these results we checked back with HRPD at room temperature and at low temperature. Apparently the result of HRPD was in accordance with XRD results. Figure 1 shows a portion of raw data diffraction patterns for samples with x = 0.27 at room temperature and 13 K. The arrow indicates the magnetic contributions as (002) and (121) and (200) in the orthorhombic crystal system with space group *Pnma* without any detectable secondary phases. The magnetic contributions are shown as extra peaks to the nuclear contributions. The result of characterization samples $La_{1-x}Ca_xMnO_3$ using HRPD with FULLPROF program at room temperature and low temperatures can be seen in Table 1.

Generally in $AMnO_3$, the A-site doping will directly change the Mn^{3+}-Mn^{4+} ratio and the exchange interaction of Mn-Mn. The lattice parameters and crystal structure will be affected due to the mismatch of the ionic radius between the Mn ions and the doping ions[8]. In $LaMnO_3$, the Mn ion have a valence 3+ (Mn^{3+}) and

Table 1. Refined parameters for $La_{1-x}Ca_xMnO_3$ with x = 0.27 and 0.47 at low temperature

		$La_{1-x}Ca_xMnO_3$			
		x = 0.27		x = 0.47	
Lattice Parameters	*a* (Å)	5.485	5.478	5.416	5.434
	b (Å)	7.760	7.751	7.635	7.633
	c (Å)	5.520	5.520	5.423	5.429
	$\alpha=\beta=\gamma$	90^o	90^o	90^o	90^o
	Vol.	234.952	233.977	224.227	222.495
	χ^2	1.35	1.53	1.47	1.47
Structure		Orthorombic Pnma	Orthorombic Pnma	Orthorombic Pnma	Orthorombic Pnma
Temperature		RT	13 K	RT	20 K
Magnetic Moment (μ_B)		-	3.10(6)	-	1.30(5)

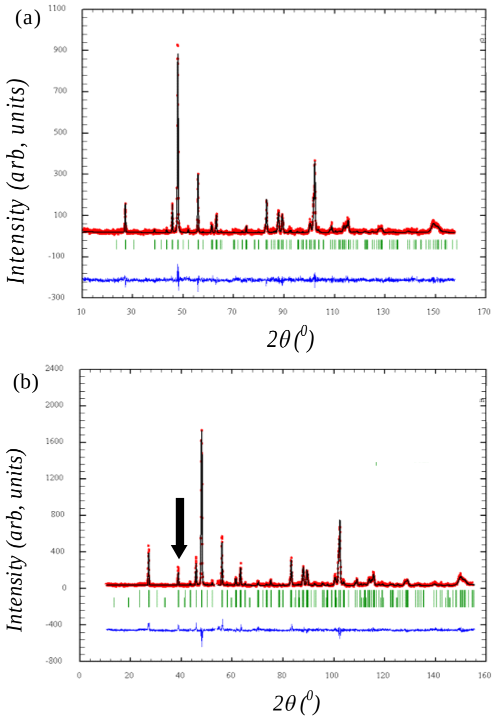

Figure 1. The result of HRPD patterns at (a). room temperature and (b). low temperature for $La_{0.73}Ca_{0.27}MnO_3$

in $CaMnO_3$, the Mn ion have a valence 4+ (Mn^{4+}), so in the $La_{1-x}Ca_xMnO_3$ the Mn ions had a mixed valence Mn^{3+} and Mn^{4+}. In the system $La_{1-x}Ca_xMnO_3$, the Ca^{2+} ions enter and move the La^{3+} ions. The emergence of the electrons in the outmost shell of Ca will be an interesting one ion of Mn^{3+}. Thus the number of Mn^{4+} that appear in the system will be equal to the amount of Ca^{2+}. Therefor the system can be written as $La^{3+}_{1-x}Ca^{2+}_xMn^{3+}_{1-x}Mn^{4+}_{1-x}O^{2-}_3$. The radius of La^{3+}, Ca^{2+}, Mn^{3+}, and Mn^{4+} is about 1.15 Å, 1.14 Å, 0.645 Å, and 0.53 Å respectively [9]. Subtitution of Ca in La will increase Mn^{4+}, causing a decrease in the volume of lattice. With increasing Ca content, the increase of the proportion of Mn^{4+} ions weakens the double exchange interaction. The same results were also obtained last experiment [10-11].

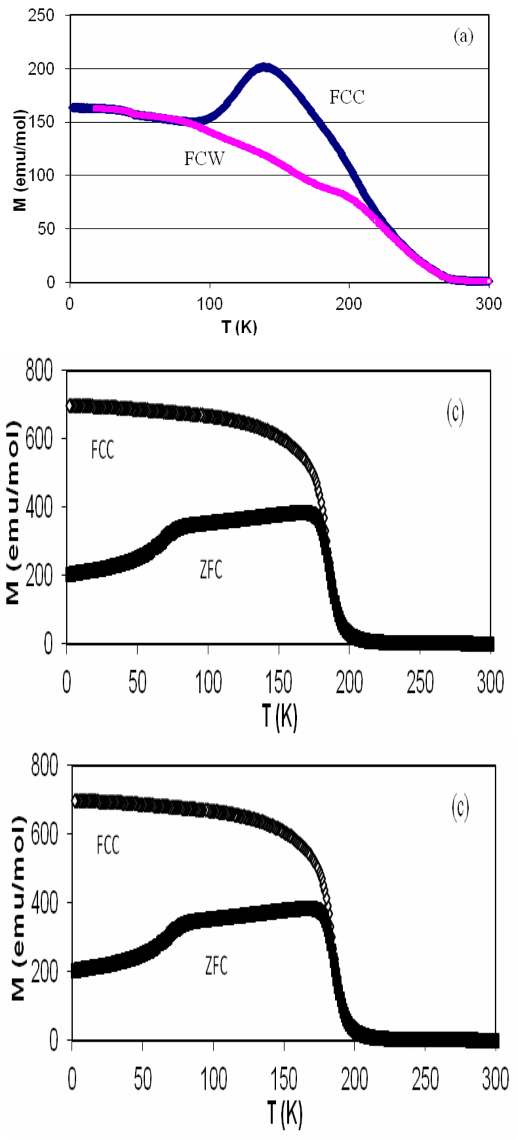

Figure 2. Temperature dependence of Magnetization for (a) upon cooling and warming (FCC and FCW) in a 20 Oersted magnetic field for $La_{0.53}Ca_{0.47}MnO_3$ (b) ZFC and FCC for $La_{0.53}Ca_{0.47}MnO_3$, and (c) $La_{0.73}Ca_{0.27}MnO_3$

Table 2. The tolerance factor $La_{1-x}Ca_xMnO_3$ (x = 0.27 and 0.47)

x	r_A (Å)	r_B (Å)	r_O (Å)	*t*
0.27	1.1358	0.6075	1.4000	0.8932
0.47	1.1453	0.5909	1.4000	0.9040

The structure of $La_{1-x}Ca_xMnO_3$ oxide is close to cubic perovskite ABO_3. The structure of manganites is governed by a tolerance factor $t=(r_A+r_O)/\sqrt{2}(r_B+r_O)$. It measures the strain in the structure resulting from a mismatch between the equilibrium A-O and B-O bond lengths. If we use the ionic radii of O^{2-} is 1.4 Å, the tolerance factors can be seen in the Table 2 below. The tolerance factor represent a strain that is typically relaxed by distortion of the structure away from its ideal cubic form (t = 1). This distortion arises from an electronic instability inherent to the Mn^{3+} ion in an octahedral crystal field of the Jahn-teller instability.

Magnetic Properties

The temperature dependence of magnetization corresponding to these materials is depicted in Figure 2. For x = 0.47, the heating and cooling M(T) curve display a hysteresis as a consequence of the mixed character of the sample, that is a mix between antiferromagnetic-ferromagnetic. The cooling process show, the temperature dependence of LCMO magnetization under a magnetic field of 2 mT. Two magnetic transitions are observed; a paramagnetism to ferromagnetism at 260 K and a ferromagnetism to antiferromagnetism at ~ 174 K.

These are typical behaviours for the charge-ordered (CO) compound. The sample to showed both a paramagnetic to ferromagnetic transition at 233 K and then an antiferromagnetic transition at 175 K [12], T_C = 225 K [13]. A small magnetization step is observed around 155 K, which suggests the existence of a weak metastable FM ordering at low temperature. The large thermal hysteresis has been reported by an other author [14,15], and may be an indication that charge ordering is a nucleation and growth process. For x = 0.27 the currie temperature is 197 K, obtained by way of plotting graphs 1/susceptibility vs temperatures see Figure 3.

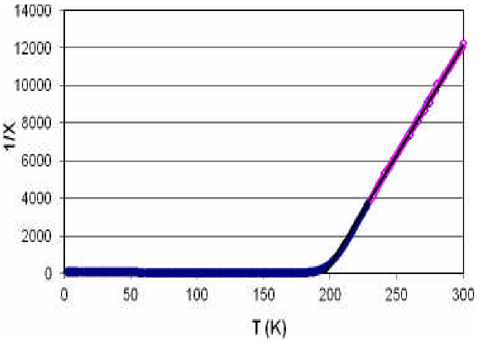

Figure 3. $1/\chi$ versus T for sample $La_{0.73}Ca_{0.27}MnO_3$

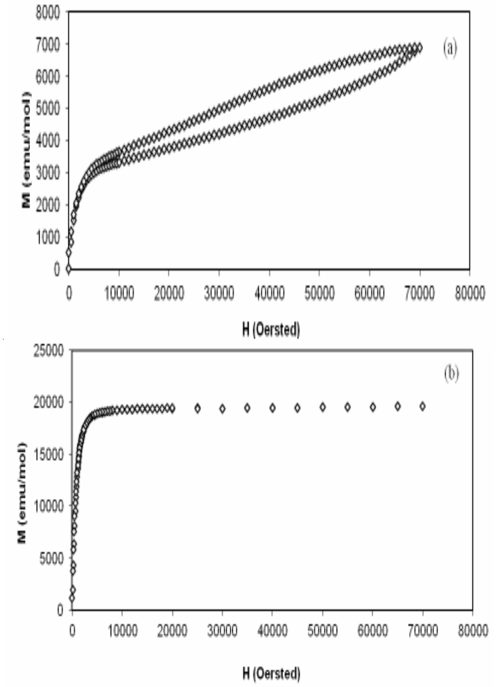

Figure 4. The external magnetic field dependence of magnetization $La_{1-x}Ca_xMnO_3$ (a) x = 0.47 and (b) x = 0.27

The analysis for the neutron-diffraction data show that for $x = 0.47$, the magnetic wave propagation vector q of $La_{0.53}Ca_{0.47}MnO_3$ is (½, 0, ½) with the magnetic moment magnitude of 1.30 μ_B is an antiferromagnetic mixed with a ferromagnetic , meanwhile for $La_{0.73}Ca_{0.27}MnO_3$ the magnetic wave propagation vector q (0,0,0) with the magnetic moment magnitude of 3.10 μ_B is a ferromagnetic in b-axis. It would be more obvious if viewed on the curve magnetization *M-H* as seen in Figure 4. In low temperature the sample $La_{0.73}Ca_{0.27}MnO_3$ is ferromagnetic. All samples have a small coercivity, showing that these samples are softmagnetic. Therefore these materials are good applications for sensors.

Figure 4 shows the field (*H*) dependence of magnetization (*M-H*) from 0-7000 Oersted at 110 K for $x = 0.47$. The step jump of magnetization in a low field indicates the existence of the FM phase. However, a rough estimate shows that the magnetization is far from saturation even when $H = 7000$ Oersted. These features suggest the coexistence of the FM phase and CO phase as a consequence of the inhomogeneous distribution of oxygen [16]. The sample $La_{0.73}Ca_{0.27}MnO_3$ shows ferromagnetic behavior and high saturation magnetization value (Figure 4(b)).

CONCLUSION

In summary, the structural and magnetic properties $La_{1-x}Ca_xMnO_3$ with $x = 0.27$ and 0.47 has been experimentally studied. Both samples have the orthorhombic structure with space group *Pnma*. Increased Ca^{2+} will add Mn^{4+}, so the volume of lattice is decreased. This will minimize the distortion of the lattice. For $x = 0.27$ exhibits a simple ferromagnetic structure with the magnetic moment 3.10 μ_B, and Tc = 197 K, while $x = 0.47$ has an antiferromagnetic mixed with a ferromagnetic with the magnetic moment 1.30 μ_B and Tc = 260 K.

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