THE EFFECT OF Cu DOPING ON CRYSTAL STRUCTURE AND MAGNETORESISTANCE IN $La_{0.73}Ca_{0.27}Mn_{1-y}Cu_yO_3$ WITH $0 < y < 0.19$

Y. E. Gunanto[1*], B. Kurniawan[2], A. Purwanto[3], Wisnu Ari Adi[3] and S. Poertadji[2]

[1]Faculty of Education, Universitas Pelita Harapan
UPH Campus, MH Thamrin Boulevard 00-00, Lippo Karawaci 1100, Tangerang 15811
[2]Department of Physics, FMIPA-UI
Kampus Baru UI, Depok 16424
[3]Center of Technology for Nuclear Industrial Materials (PTBIN)-BATAN
Kawasan Puspiptek, Serpong 15314, Tangerang Selatan
e-mail : yohanes.gunanto@uph.edu; ye_gunanto@yahoo.com

ABSTRACT

THE EFFECT OF Cu-DOPING ON CRYSTAL STRUCTURE AND MAGNETORESISTANCE IN $La_{0.73}Ca_{0.27}Mn_{1-y}CuyO_3$ WITH $0 < y < 0.19$. We studied the crystal structure at room temperature and low temperature, as well as the magnetoresistance as a function magnetic field at room temperature in the compound $La_{0.73}Ca_{0.27}Mn_{1-y}Cu_yO_3$ with $0 < y < 0.19$. To analyze the crystal structure we used X-Ray Diffractometer (XRD) at room temperature and the neutron-powder-diffraction at room temperature and low temperatures. The neutron powder diffraction experiments were under taken with the High Resolution Powder Diffractometer (HRPD) (λ=1.8223 Å) at the Neutron Scattering Center of BATAN using the fullprof program. To analyze the magnetoresistance, we used a four point probe aparatus in the range of magnetic fields 0-7600 Oersted. we have found that no change in crystal structure despite of increasing value of *y*. All samples have structure *orthorhombic* with space group *P nma,* but the volume of lattice in low temperature is smaller than room temperature. At room temperature, increasing the value *y* impact declining value of magnetoresistance.

Keywords: Crystal structure, HRPD, Fullprof program, Magnetoresistance

ABSTRAK

PENGARUH DOPING Cu PADA STRUKTUR KRISTAL DAN *MAGNETORESISTANCE* $La_{0.73}Ca_{0.27}Mn_{1-y}Cu_yO_3$ DENGAN $0 < y < 0,19$. Telah dipelajari struktur kristal pada suhu kamar dan suhu rendah dan magnetoresistansi sebagai fungsi medan magnet pada suhu kamar pada senyawa $La_{0.73}Ca_{0.27}Mn_{1-y}Cu_yO_3$ dengan $0 < y < 0,19$. Untuk menganalisis struktur kristal pada suhu kamar digunakan *X-Ray Diffractometer (XRD)* dan pada suhu rendah digunakan difraksi neutron. Pengukuran dengan difraksi neutron dilakukan dengan *High Resolution Powder Diffractometer* (*HRPD*) (λ=1,8223 Å) di pusat hamburan neutron BATAN menggunakan program *fullprof*. Untuk menganalisis magnetoresistansi digunakan *four point probe* dalam rentang medan magnet 0 *Oersted* hingga 7600 *Oersted*. Dengan bertambahnya nilai y, maka tidak ada perubahan struktur kristal. Namun volume kisi pada suhu rendah lebih kecil bila dibandingkan dengan volume kisi pada suhu kamar. Pada suhu kamar, semakin bertambah nilai y, maka semakin berkurang magnetoresistansinya.

Kata kunci: Struktur kristal, *HRPD*, Program *fullprof*, Magnetoresistansi

INTRODUCTION

Manganate perovskite compound of rare earth oxides with general formula $A_{1-x}B_xMnO_3$, where A = trivalent rare earth atoms and B = divalent transition metal atoms is one of the compounds that are very attractive for researchers in the past decade. These compounds show unique physical and magnetic properties, which until now has not been fully resolved, such as the nature magnetoresistance [1]. This interest is even increasing with the development of Cu doping of Mn [2-12]. The Cu substitution on

Mn is very interesting because there are still differences in resistivity values, get resisitivitas value to drop dramatically when Cu replaces the 5% Mn, while get a tremendous increase in resistance [13,14]. The crystal structure can be orthorhombic [1,9] or rhombohedral [12].

In this study, it carried out through diffraction of X-Rays and High Resolution Powder Diffraction (HRPD) known crystal structure, while for the magnetoresistance analysis at room temperature used four point probe.

EXPERIMENTAL METHOD

The samples were prepared by solid state reaction of $CaCO_3$, La_2O_3, MnO_2, and CuO of at least 99.99% purity. We performed some preliminary works and it was noted that any treatment below 1000 °C would not result any single phase sample. 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 ball milling and heating were carried out in the air environment.

The phase purity was checked by a powder X-Ray Diffraction, which indicated a single-phase character of sample. The neutron-powder-diffraction experiments were undertaken with the high-resolution powder diffractometer HRPD (λ=1.8223 Å) at the Neutron Scattering Laboratory of BATAN, Serpong, Indonesia. The samples were loaded in a cylindrical vanadium can and placed in a helium cryostat. The data were collected in the scattering angular range of 2.5° up to 157° in the interval of 0.05° for the low and room temperature measurements.

The resistivity measurements performed at room temperature using four point probe with electric current 50 mA and the voltage variation of
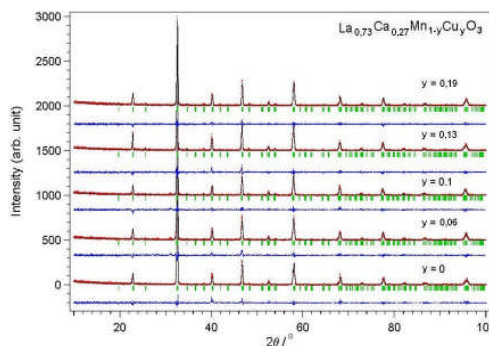

Figure 1. Refined of XRD for $La_{0.73}Ca_{0.27}Mn_{1-y}Cu_yO_3$ at room temperature.

DC 0-12 volt. The magnetic field are in the range between 0-7600 Oersted.

RESULT AND DISCUSSION

Crystal Structure

The result of measurement of crystallographic structure at room temperature and low temperature by using XRD as can be seen from Figure 1. All peaks can be indexed well, so that sample showed one phase. Samples have orthorhombic crystal structure with space group Pnma. The same result when used High Resolution Powder Diffraction (HRPD) either at room temperature or low temperature. The magnetic contributions are shown as extra peaks to the nuclear contribution.

The result of refined structural parameters at room temperature and low temperature as can be seen from Table 1. At room temperature, for y = 0.06 and 0.13, the unit cell volumes were less than the one without Cu (y = 0). On the other hand, for y = 0.10 and 0.19 the unit cell volumes were greater than the one without doping. At low temperature, the unit cell volumes increase along with the addition of Cu, except for y = 0.13.

Table 1. The lattice parameters of $La_{0.73}Ca_{0.27}Mn_{1-y}Cu_yO_3$ (0 < y < 0.19) at room temperature and low temperatures.

		$La_{0.73}Ca_{0.27}Mn_{(1-x)}Cu_{(x)}O_3$								
		x = 0		*x* = 0.06		*x* = 0.10		*x* = 0.13		*x* = 0.19	
Parameter Kisi	a	5.484	5.477	5.484	5.479	5.494	5.491	5.484	5.480	5.492	5.488
	b	7.760	7.750	7.761	7.753	7.777	7.765	7.757	7.750	7.772	7.764
	c	5.520	5.511	5.520	5.508	5.519	5.506	5.511	5.504	5.513	5.506
	α	90		90		90		90		90	
	β	90		90		90		90		90	
	γ	90		90		90		90		90	
	Vol	234.908	233.977	234.943	234.033	235.809	234.830	234.434	233.790	235.359	234.669
	χ^2	1.36	1.53	1.16	1.38	1.45	1.51	1.49	1.46	1.92	1.34
Struktur		*orthorombic*		*orthorombic*		*orthorombic*		*orthorombic*		*orthorombic*	
		P nma		*P nma*		*P nma*		*P nma*		*P nma*	
Temperatur		RT	13 K	RT	13 K	RT	19 K	RT	21 K	RT	14 K

Generally, the B-site doping will directly change the Mn^{3+} - Mn^{4+} ratio. The lattice parameters and crystal structure will be affected due to the mismatch of ionic radius between the Mn ions and the doping ions. Doping value of Cu between 0-0.2, crystal will have rhombohedra structure [4]. On the other hand, for doping between 0.3-0.5, crystal will have orthorhombic structure. Cu^{2+} ions have radius about 0.73Å, which is much larger than the radius of Mn^{3+} (0.645 Å) and Mn^{4+} (0.53 Å) ions [15]. The substitution of Mn by Cu^{2+} will cause expansion of the unit cells volume. We obstained on previous results, which on samples of $La_{0.1}Ca_{0.9}Mn_{1-x}Cu_xO_3$ [16] indicating the entire Cu in Cu^{2+}, but in this study the data show that not all unit cells volume samples increase. Therefore, the decrease of the unit cell volume with Cu-Doping at RT suggests that some of the Cu ions are in a Cu^{3+} state with a radius 0.54 Å (less than the radius of Mn^{3+}, but greater than the radius of Mn^{4+}). The same result that Cu^{2+} and Cu^{3+} coexist with the dominant Cu^{2+} state. Until now, the effect of Cu doping still very attracted the attention of some researchers [2].

Suppose y describe proportion of Mn^{4+} and z describe proportion of Cu^{3+}, then the sample composition by Cu = 0.13 can be written as $La_{0.73}Ca_{0.27}Mn^{3+}_{0.87(1-y)}Mn^{4+}_{0.87y}$ $Cu^{2+}_{0.13(1-z)}Cu^{3+}_{0.13z}O_3$. The Cu $2p_{3/2}$ binding energy become a broadened peak at higher energy levels [2]. This higher binding energy arises from Cu being in a higher oxidation state of 3+ (Cu^{3+}). The proportion of Cu^{3+} is 12% and 20% for 0.20 Cu doping 0.15 and 0.20 respectively and the proportion of Mn^{4+} ions is 50% (y = 0.15) and 57% (y = 0.20). Meanwhile, found the content of Cu^{3+} which could amount to ~60% of the total Cu doping content [9].

As a result, the proportion of Cu^{3+} is 60% for y = 0.15. There are many controversial results had been report regarding to the effect of Cu doping in Mn that still can be further investigated. Even so, all of research results show that the increase of Cu amount will also increase the amount ions of Mn^{4+} that resulting in weakening of double exchange interaction. If we refer to the result of M.S.Kim *et al* [2], we get the portion of Mn^{4+} are 45% (y = 0.13) and 53% (y = 0.19). At low temperature, the result is almost the same as the result of at RT. Unit cell volume is increase along with the increase amount of Cu, except for Cu = 0.13 doping value. This becomes very interesting and require further analysis. Lattice volume at low temperature is less than the one at RT.

Magnetoresistance

Resistivity measurement was done with four pint probe, electric current 50 mA at RT and outer magnetic field 0-7600 Oersted. Magnetoresistence is defined as, Equation (1)
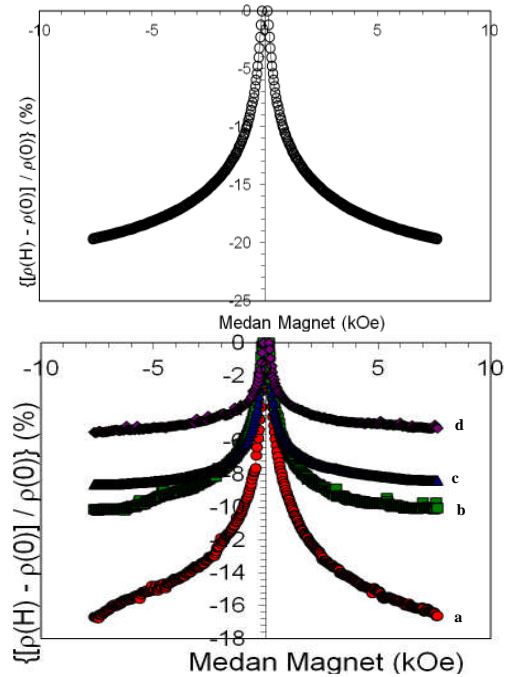

Figure 2. The magnetoresistance vs the external magnetic field without Cu-doping (above) and with Cu-doping (a) y = 0,06, (b) y = 0,10, (c) y = 0,13, dan (d) y = 0,19 (under).

$$MR(\%) = \frac{R(H) - R(0)}{R(0)} \, x100\% \quad \cdots\cdots\cdots\cdots \quad (1)$$

Where:
R(0) = Represent the electric resistance when magnetic field 0
R(H) = Represent the electric resistance when magnetic field H (in this case the maximum value of H is 7600 Oersted).

The result of magnetoresistence can be seen from Figure 2. Sample without Cu-Doped, magnetoresistence maximum at RT about 20%, while others with Cu-Doped were 17% (y=0.06), 10% (y=0.10), 8% (y=0.13), and 5% (y=0.19) respectively. With increasing Cu content, the magnetic moment of compound decrease. The same result also found by researcher [13]. However, Ghosh *et al,* got result that the value of magnetoresistence will increase along with the increase amount of Cu which is done in low temperature, close to its Currie. This was not done by us because of the limitation of facility. We guess that the high value of sample magnetoresistence because it was in ferromagnetic state or mixed with anti ferromagnetic. While at RT, it was paramagnetic.

Ca-doped in La caused *hole* for Mn position because the La outer shell has 3 electrons, while Ca has 2 electrons. Therefore, electron able to move from Mn^{3+} ions to oxygen ions and at the same time, others electrons move from oxygen ions to Mn^{4+} ions. This process is called as *double exchange* mechanism. The possibility of this transfer depends on magnetic spin orientation of Mn ions. If Mn ions spin not in the same direction, the

moving electron will lose its kinetic energy. This is happen as the consequences of electron spin that always adjust with the spin of ions. Resistance will decrease or manganite conductivity will increase if Mn ions spin move in the same direction. This condition can be made by refrigeration or adding external magnetic field.

The Cu^{3+} has 8 electrons in *d* orbital that is localized by strong coulomb repulsive force. Therefore, Cu substitution will weaken *double exchange* interaction [7].

CONCLUSIONS

Based on the obtain result, we may conclude that :

1. The Cu doping does not change the crystallographic structure. All sample had orthorhombic structure with Pnma group space.
2. The Cu-doping in Mn ($Cu^{2+} = 0.73$ Å), will increase the volume of a lattice, but if the state of Cu in Cu^{3+} (0.54 Å) then the volume of lattice will slightly decrease, because the radius of Cu^{3+} smaller than Mn^{3+} (0.645 Å), but greater than Mn^{4+} (0.53 Å).
3. In room temperature, greater Cu doping effect due to Mn will result in decreasing of magnetoresistance value.

REFERENCES

[1]. M. PISSAS, I. MARGIOLAKI, K. PRASSIDES and E. SUARD, *Phys. Rev. B*, **72** (064426) (2005)

[2]. M. S. KIM, J. B. YANG, J. MEDVEDEVA, W. B. YELON, P. E. PARIS and W. J. JAMES, *J. Phys. Condens. Matter.*, **20** (255228) (2008)

[3]. P.KUMAR and R.K.DWIVEDI, *Journal of the Korean Physical Society*, **58** (1) (2011) 58-63

[4]. M. EL-HAGARY, Y. A. SHOKER, S. MOHAMMAD, A. M. MOUSTAFA, A. ABD EL-AAL, H. MICHOR, M. REISSNER, G.HILSCHER and A. A. RAMADAN, *J. Alloys Compd.*, (2008)

[5]. N.BISKUP, A.DE ANDRES, N.M.NEMES, M.G.HERNADEZ, K.V.GLAZYRIN and Y.M.MUKOVSKII, *Applied Physics Letter*, **90** (222502) (2007)

[6]. M. L.CRAUS and M. LOZOVAN, *Journal of Optolectronic and Advance Materials*, **8** (3) (2006) 1008-1011

[7]. M. S. KIM, J. B. YANG, P. E. PARRIS, Q. CAI, X. D. ZHOU, W. J. JAMES, W. B. YELON, D. BUDDHIKOT and S. K. MALI, *J. Appl. Phys.*, **97** (10H714) (2005)

[8]. N. CHAU, P. Q. NIEM, H. N. NHAT, N. H. LUONG and N. D. THO, *Phisica B*, **327** (2003) 214-217

[9]. H. -D. ZHOU, G.LI, X. -Y.XU, S. -J.FENG, T. QIAN and X.-G.LI, *Materials Chemistry and Physics*, **75** (2002) 140-143

[10]. K. Y. WANG, W. H. SONG, J. M. DAI, S. L. YE, S. G.WANG, Y. P. SUN and J. J. DU, *Phys. Stat. Sol.* (a), **184** (2) (2001) 515-522

[11]. S. L. YUAN, Z. Y. LI, X.Y. ZENG, G. Q. ZHANG, F. TU, G. PENG, J. LIU, Y. JIANG, Y. P. YANG and C. Q. TANG, *Eur. Phys. J. B*, **20** (2000) 177-181

[12]. A. I.TOVSTOLYTKIN, A. N. POGORILYI, A. G. BELOUS and O. Z.YANCHEVSKI, *Low Temperature Physics*, **27** (5) (2001) 366-371

[13]. K. GHOSH, S. B. OGALE, R. RAMESH, R. L. GREENE, T. VENKATESAN, K. M. GAPCHUP, RAVI BATHE and S. I. PATIL, *Phys. Rev. B*, **59** (1999) 533-537

[14]. LI PI, L. ZHENG and Y. ZHANG, *Phys. Rev. B*, **61** (8917) (2000)

[15]. R. D. SHANNON, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, **32** (751) (1976)

[16]. Y. E. GUNANTO, B. KURNIAWAN, A. PURWANTO and W. A. ADI, *Indonesian Journal Science of Materi*, **Special Edition** (Oktober) (2007) 72-76