



Chiang Mai J. Sci. 2018; 45(5) : 2026-2033

<http://epg.science.cmu.ac.th/ejournal/>

Contributed Paper

Room Temperature Ferromagnetism Observed in Co-doped LaTiO_3 Nanofibers Fabricated by Electrospinning and Calcination

Wichaid Ponhan*, Apirak Choonlasri, Aekkachai Phontham and Pornchai Chinnasa

Program of Physics, Faculty of Science and Technology, Rajabhat Maha Sarakham University,

Maha Sarakham 44000, Thailand.

* Author for correspondence; e-mail: wichaid.po@rmu.ac.th; wichaidponhan@gmail.com

Received: 1 November 2017

Accepted: 30 April 2018

ABSTRACT

In this study, $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers with $x = 0, 0.025, 0.05, 0.075$ and 0.1 were fabricated by electrospinning technique and calcination. The $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers with average diameters of $\sim 135 - 186$ nm were successfully obtained from calcination of the as-spun $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3/\text{PVP}$ nanofibers at 1000°C in argon for 2 h. The calcined $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers were characterized by a variety of techniques. X-ray diffraction and transmission electron microscopy studies indicated all samples calcined at 1000°C are a single phase of cubic perovskite structure with no secondary magnetic phase in this study. All of the samples with $x = 0, 0.025, 0.05, 0.075$ and 0.1 are found to be ferromagnetic at room temperature. With the increasing of x , the ferromagnetism was increased. The structural defect such as oxygen vacancies may play an important role to induce room temperature ferromagnetism in $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers.

Keywords: $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$), nanofibers, electrospinning, dilute magnetic oxide, ferromagnetic

1. INTRODUCTION

Recently, the research of ferromagnetic semiconductors is an important challenge in spintronics nowadays. Since the room temperature ferromagnetism (RTFM) was found in Mn-GaAs [1], several types of other diluted magnetic semiconductors have been investigated [2-7]. The result of room temperature ferromagnetism in Co-doped TiO_2 [8] has started an intense research on other diluted magnetic oxide systems (DMOs). Some recent experiment has been reported

room temperature ferromagnetism in perovskite of Co-doped $(\text{La,Sr})\text{TiO}_{3-\delta}$ nanoparticles and thin films [9-13]. Wongsaprom et al [11] reported the existence of ferromagnetism in Co-doped $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_{3-\delta}$ fabricated by a polymerized complex (PC) method. The specific saturation magnetization (M_s) values of 0.038 emu/g was observed for the sample calcined at 800°C which provides strong indication that Co-doped $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_{3-\delta}$ nanoparticles

display RTFM. In Fe-doped $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_{3.8}$ system, the undoped samples are diamagnetic, whereas the Fe-doped samples show ferromagnetism at room temperature [12]. Herranz et al [10] demonstrate the existence of a significant spin polarization in Co-doped $(\text{La}, \text{Sr})\text{TiO}_{3.8}$, a ferromagnetic diluted magnetic oxide system with high Curie temperature by using low-oxygen pressure growth conditions. Up to date, most studies reported on Co-doped $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_{3.8}$ has been fabricated in different morphology such as thin films, powder, or nanoparticles which prepared by several method. No studies report on the fabrication and magnetic properties of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers. The finding of room temperature ferromagnetism in $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers would allow an enhanced flexibility for applications in nanotechnology.

In this paper, we report the room temperature ferromagnetism observed in Co-doped LaTiO_3 nanofibers fabricated by electrospinning with average diameters of $\sim 135 - 186$ nm. The prepared $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy. The room temperature magnetic properties of the samples were also investigated by Vibrating sample magnetometer (VSM).

2. MATERIALS AND METHODS

In a typical procedure, Lanthanum (III) nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), were mixed with 5 ml of diisopropoxytitanium bis(acetylacetonate) solution, 22.5 ml of dimethylformamid and 2.5 ml of deionized water. After being magnetically stirred for 3 h, this mixture was mixed with the solution containing 27 ml of ethanol and 3 g of PVP (Aldrich, $M_w \approx 1300000$) until a homogeneous solution was obtained.

Then, this mixture was loaded into a plastic syringe equipped with a 22-gauge needle made of stainless steel. The electrospinning process was carried out using our home-made electrospinning system. The needle was connected to a high-voltage supply. The solution was fed at a rate of 1.0 ml/h using a syringe pump. A piece of flat aluminum foil was placed 16 cm below the tip of the needle, and used to collect the nanofibers. The high voltage for electrospinning was 17.5 kV applied between the tip of needle and ground collector. All electrospinning processes were carried out at room temperature. The PVP was selectively removed by calcination the as-spun ($\text{LaTi}_{1-x}\text{Co}_x\text{O}_3/\text{PVP}$ ($0 \leq x \leq 0.1$)) nanofibers in argon for 2 h at 1,000 °C. The morphology of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers was characterized by SEM (LEO SEM 1450VP, UK), TEM (FEI Tecnai G2 F20 FE-TEM, Netherland). A measurement of all fibers taken from SEM micrographs was used to determine average fiber diameter and distribution. Powder X-ray diffraction (XRD) was used for crystal phase identification and estimation of the crystallite size. The X-ray diffraction measurements were performed on a PANalytical Empyrean. The magnetic properties of the samples were examined at room temperature using a vibrating sample magnetometer (VSM) (VersaLab, QuantumDesign).

3. RESULTS AND DISCUSSION

The morphology of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers was revealed by SEM. Figure 1 shows the SEM micrographs with respective diameter histograms of the $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers. The calcined nanofibers appeared quite smooth, each individual nanofiber was quite uniform in cross section, and the average diameter of the fiber was $\sim 135 - 186$ nm. The PVP

was selectively removed by calcinations the as-spun nanofibers in argon for 2 h at the same temperature (1000 °C). All of the calcined samples formed a structure of packed particles or crystallites. These changes in the morphology are related to a dramatic change in crystal structure as observed in electrospun TiO_2 [14], NaCo_2O_4 [15], ZnFe_2O_4 [16], CuFe_2O_4 [17], $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$

[18], $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [19], $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ [20]. For $x = 0, 0.025, 0.05, 0.075$ and 0.1 , the nanofibers are remained as continuous structures after calcined at 1000 °C as shown in Figure 1, and their average diameter are 135 ± 25 , 171 ± 18 , 186 ± 14 , 175 ± 19 and 136 ± 17 nm, respectively (as shown in Table 1).

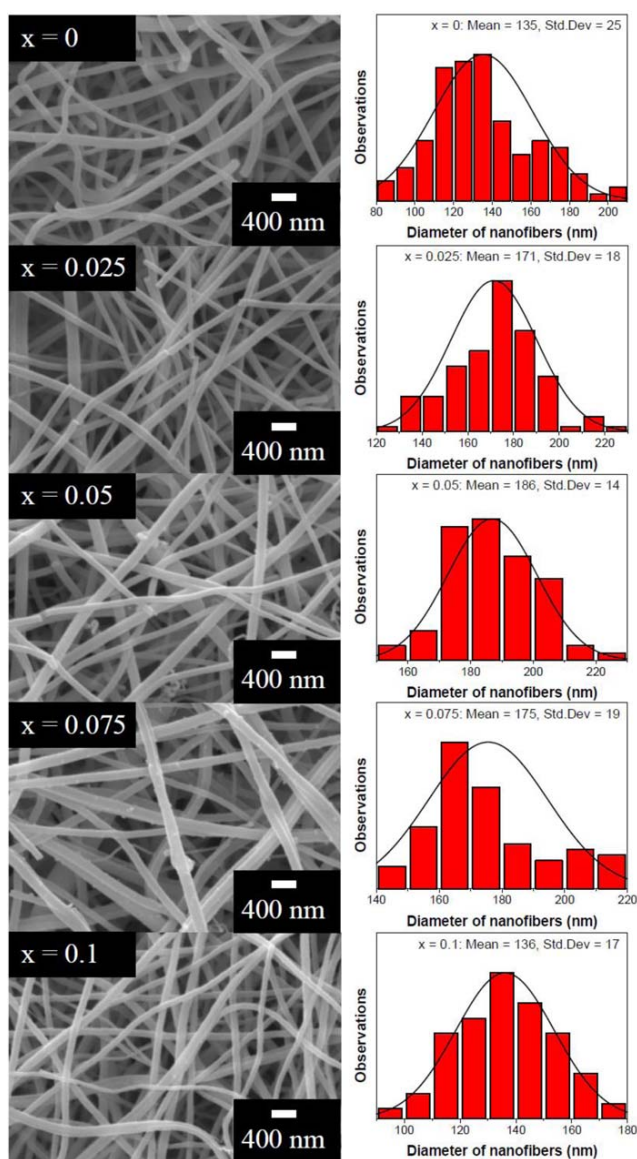


Figure 1. SEM micrographs and histogram showing the size distribution of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers calcined in argon at 1000 °C for 2 h.

Table 1. Average crystal sizes from XRD line broadening, lattice parameter a , average fibers diameter from SEM of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers calcined in argon at 1000 °C for 2 h.

Sample	Average crystal size from XRD (nm)	Lattice parameters a , (nm)	Average fiber diameter (nm)	M_s at 30 kOe (emu/g)
$x = 0$	8.2 ± 0.7	0.3930 ± 0.0003	135 ± 25	0.18
$x = 0.025$	7.8 ± 1.7	0.3928 ± 0.0003	172 ± 18	0.40
$x = 0.05$	8.3 ± 1.1	0.3944 ± 0.0006	186 ± 14	1.07
$x = 0.07$	8.3 ± 1.5	0.3944 ± 0.0005	175 ± 19	1.75
$x = 0.1$	7.6 ± 0.9	0.3943 ± 0.0006	136 ± 17	2.33

The detailed morphology and crystalline structure of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers were further investigated by TEM. Figure 2 shows TEM bright field images with corresponding selected-area electron diffraction (SAED) of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers calcined in argon at 1000 °C for 2 h. All of samples show spotty ring pattern including the reflection of (110), (111), (200), (210) and (211) of cubic perovskite structure with no secondary phase that is similar to those observed in $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [11-12, 19] and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ [20]. All of TEM bright field images show the nanofibers with diameter of ~100-200 nm that corresponding to the results of SEM in Figure 1.

The XRD patterns of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers calcined at 1000 °C are shown in Figure 3, all of the main peaks are indexed as the cubic perovskite LaTiO_3 in the standard data (Reference code: 01-075-0267) that similar to those observed in $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [11-12, 19] and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ [20], and agreement with the TEM results. Since no diffraction peaks corresponding to Ti precipitates, La_2O_3 , or Co-related impurity phases such as Co, CoO, Co_2O_3 , or Co_3O_4 were observed in the Co-doped LaTiO_3 samples, it is further confirmed the formation of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ solid solution

without Co precipitation or any secondary phases. The average crystallite sizes of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ samples were calculated from X-ray line broadening of reflection of (110), (111), (200), and (210) using Scherrer's equation [21], and were found to be 8.2 ± 0.7 , 7.8 ± 1.7 , 8.3 ± 1.1 , 8.3 ± 1.5 and 7.6 ± 0.9 nm for the samples of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers calcined in argon for 2 h at $x = 0, 0.025, 0.05, 0.075$ and 0.1 , respectively. The values of lattice parameters a calculated from the XRD spectra were $a = 0.3930 \pm 0.0003$, 0.3928 ± 0.0003 , 0.3944 ± 0.0006 , 0.3944 ± 0.0005 and 0.3943 ± 0.0006 nm for the samples of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers at $x = 0, 0.025, 0.05, 0.075$, and 0.1 , respectively. The lattice parameters a for all samples are close to the value 0.3920 nm in the standard data (Reference code: 01-075-0267) and to those reported by Sunstrom et al (1992) [22], however, the value are higher than the standard data (> 0.3920 nm), indicating Ti^{3+} proportion in LaTiO_3 nanofibers are higher than the value of standard data (LaTiO_3). The crystallite sizes and lattice parameters of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers are also summarized in Table 1. On the basis of all characterization results, it seems reasonable to consider that Co impurity had been incorporated into the lattice of the LaTiO_3 nanofibers.

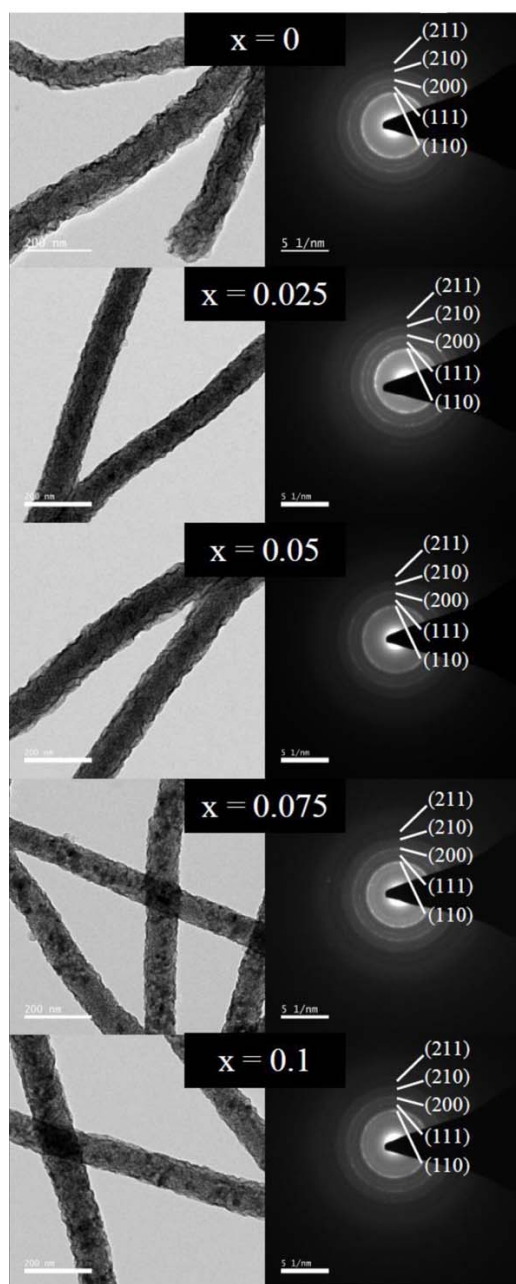


Figure 2. TEM bright-field images with corresponding selected-area electron diffraction (SAED) of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers calcined in argon at 1000°C for 2 h.

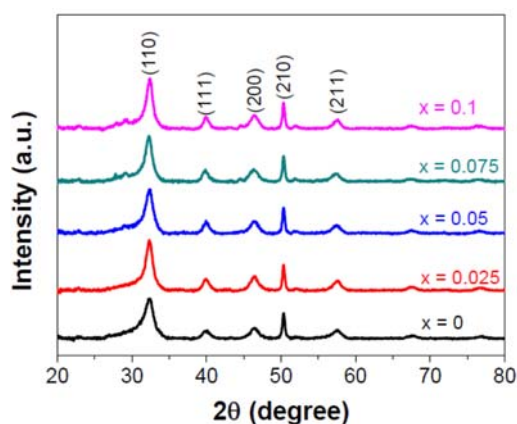


Figure 3. (a) XRD patterns of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers calcined in argon at 1000°C for 2 h.

The specific magnetization curves of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers obtained from room temperature VSM measurement are shown in Figure 4. The sample of calcined nanofibers ($x = 0$) present a weak ferromagnetic behavior which is an interested result because this ferromagnetic behavior are different to those observed diamagnetism in LSTO nanoparticles (Maensiri et al., 2007 [12]; Wongsaprom et al., 2007 [11]; Wongsaprom, 2009 [23]) which synthesized by the polymerized complex (PC) method and in bulk LSTO (Wongsaprom et al., 2010 [24]). These phenomena similar to the present of ferromagnetism in non magnetic materials such as CaO (Elfimov et al., 2002 [25]), ZnO (Patterson, 2006) [26] and $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [19].

From Figure 4, all of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.025, 0.05, 0.075$ and 0.1) nanofibers show ferromagnetic behavior, have clear hysteresis ferromagnetism in the field rang of ± 5 kOe. These ferromagnetic behaviors are similar to those observed ferromagnetism in

$\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ nanoparticles [12] which synthesized by the polymerized complex (PC) method and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Ni}_x\text{O}_3$ nanofibers [20] which fabricated by the electrospinning method. The specific magnetization (M_s) of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers increase with increasing Co concentration (increase x) and have a specific magnetization value at 30 kOe are 0.40, 1.07, 1.75, and 2.33 emu/g for $x = 0.025, 0.05, 0.075,$ and $0.1,$ respectively. It is suggested from these results that the $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ samples calcined at $x = 0.1$ have the highest M_s . Herranz et al [10, 27] observed the saturation magnetization of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{0.98}\text{Co}_{0.02}\text{O}_{3-\square}$ thin films to be 4.5 emu/cm^3 and found to be increased when the oxygen pressure decreased. They suggested that oxygen vacancies play an important role on magnetism. In general, oxygen vacancies can easily exist at the surface more than inside of a sample. Thus, in this report, oxygen vacancies would exist at the surface of the nanofibers. However, limitation of the deep of oxygen vacancies from the surface of the nanofibers is still unclear [19]. As a result from Figure 1, the $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers have a scaffolds structure with high porosity between the fibers, and no agglomerates. During calcination, argon has more chance to contact with the nanofibers and this limits the amount of oxygen, thus inducing more oxygen vacancies in the nanofibers. Therefore, the observed of M_s in our $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers is possibly attributed to oxygen content. These results suggested that there are some oxygen vacancies in the nanofibers and these oxygen vacancies are the main cause that can lead to induce room temperature ferromagnetism in $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ nanofibers [19-20, 28-30]. From Figure 4, the coercive forces (H_c) were obtained to be 465, 536, 424 and 423 Oe for the $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers at $x = 0.025, 0.05, 0.075$ and $0.1,$ respectively.

The values of specific magnetization M_s at 30 kOe of all samples are also summarized in Table 1.

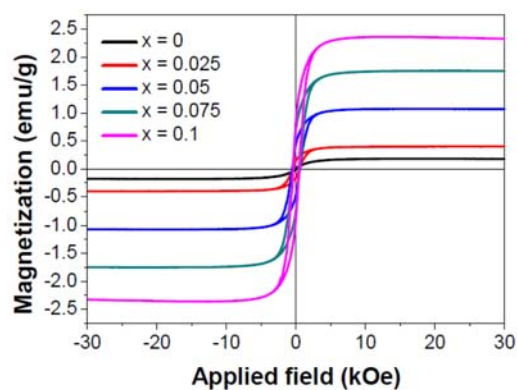


Figure 4. The specific magnetization at room temperature measured by VSM of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers calcined in argon at $1000 \text{ }^\circ\text{C}$ for 2 h.

4. CONCLUSIONS

$\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.1$) nanofibers have been successfully fabricated using an electrospinning technique and calcination. The $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers with single phase of cubic perovskite structure were obtained after calcinations at $1000 \text{ }^\circ\text{C}$ in argon for 2 h. The average diameter of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers after calcined at the same temperature ($1000 \text{ }^\circ\text{C}$) are $\sim 135 - 186 \text{ nm}$. Room temperature magnetization results showed ferromagnetic behavior and the values increase with increasing Co impurity, having the specific magnetizations of 0.40, 1.07, 1.75, and 2.33 emu/g at 30 kOe for the $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers at $x = 0.025, 0.05, 0.075$ and $0.1,$ respectively. The oxygen vacancies may play an important role to induce room temperature ferromagnetism in $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$ nanofibers. This work demonstrates that a simple method can be used to fabricate the nanofibers of $\text{LaTi}_{1-x}\text{Co}_x\text{O}_3$, which may potentially be useful for nanotechnology applications such as spintronics.

ACKNOWLEDGEMENTS

The authors would like to thank Assoc. Prof. Dr. Supree Pinitsoontorn for providing VSM, Faculty of Science, Khon Kaen University for providing SEM and TEM. This research was supported by the Research and Development Institute, Rajabhat Maha Sarakham University.

REFERENCES

- [1] Ohno H., Shen A., Matsukura F., Oiwa A., Endo A., Katsumoto S. and Lye Y., *Appl. Phys. Lett.*, 1996; **69(3)**: 363-365. DOI 10.1063/1.118061.
- [2] Chambers S.A., Droubay T., Wang C.M., Lea A.S., Farrow R.F.C., Folks L., Deline V. and Anders S., *Appl. Phys. Lett.*, 2003; **82(8)**: 1257-1259. DOI 10.1063/1.1556173.
- [3] Manivannan A., Glaspell G. and Seehra M.S., *J. Appl. Phys.*, 2003; **94(10)**: 6994-6996. DOI 10.1063/1.1622991.
- [4] Wang Z.J., Tang J.K., Tung L.D., Zhou W.L. and Spinu L., *J. Appl. Phys.*, 2003; **93(10)**: 7870-7872. DOI 10.1063/1.1556122.
- [5] Kim J.H., Kim H., Kim D., Ihm Y.E. and Choo W.K., *J. Appl. Phys.*, 2002; **92(10)**: 6066-6071. DOI 10.1063/1.1513890.
- [6] Stampe P.A., Kennedy R.J., Xin Y. and Parker J.S., *J. Appl. Phys.*, 2003; **93(10)**: 7864. DOI 10.1063/1.1556119.
- [7] Wang Z., Tang J., Chen Y., Spinu L., Zhou W. and Tung L.D., *J. Appl. Phys.*, 2004; **95(11)**: 7384-7386. DOI 10.1063/1.1667858.
- [8] Matsumoto Y., Murakami M., Shono T., Hasegawa T., Fukumura T., Kawasaki M., Ahmet P., Chikyow T., Koshihara S. and Koinuma H., *Science*, 2001; **291(5505)**: 854-856. DOI 10.1126/science.1056186.
- [9] Zhao Y.G., Shinde S.R., Ogale S.B., Higgins J., Louand S.E., Lanci C., Buban J.P., Browning N.D., Das Sarma S., Millis A.J., Kulkarni V.N., Choudhary R.J., Greene R.L. and Venkatesan T., *Appl. Phys. Lett.*, 2003; **83(11)**: 2199-2201. DOI 10.1063/1.1610796.
- [10] Herranz G., Ranchal R., Bibes M., Jaffres H., Jacquet E., Maurice J.L., Bouzehouane K., Wyczisk F., Tafra E., Basletic M., Hamzic A., Colliex C., Contour J.P., Barthelemy A. and Fert A., *Phys. Rev. Lett.*, 2006; **96(2)**: 027207(1-4). DOI 10.1103/PhysRevLett.96.027207.
- [11] Wongsaprom K., Swatsitang E., Maensiri S., Srijaranai S. and Seraphin S., *Appl. Phys. Lett.*, 2007; **90(16)**: 162506(1-3). DOI 10.1063/1.2724772.
- [12] Maensiri S., Wongsaprom K., Swatsitang E. and Seraphin S., *J. Appl. Phys.*, 2007; **102(7)**: 076110(1-3). DOI 10.1063/1.2786674.
- [13] Ranchal R., Bibes M., Barthelemy A., Bouzehouane K., Guyard S., Jacquet E., Contour J.P., Passcanut C., Berthet P. and Dragoe N., *J. Appl. Phys.*, 2005; **98(1)**: 013514(1-5). DOI 10.1063/1.1938278.
- [14] Nuansing W., Ninmuang S., Jareerboon W., Maensiri S. and Seraphin S., *Mater. Sci. Eng. B*, 2006; **131(1-3)**: 147-155. DOI 10.1016/j.mseb.2006.04.030.
- [15] Maensiri S. and Nuansing W., *Mater. Chem. Phys.*, 2006; **99(1)**: 104-108. DOI 10.1016/j.matchemphys.2005.10.004.
- [16] Ponhan W., Swatsitang E. and Maensiri S., *Mater. Sci. Technol.*, 2010; **26(11)**: 1298-1303. DOI 10.1179/026708310X12798718274115.
- [17] Ponhan W. and Maensiri S., *Solid State Sci.*, 2009; **11(2)**: 479-484. DOI 10.1016/j.solidstatesciences.2008.06.019.

- [18] Maensiri S., Nuansing W., Klinkaewnarong J., Laokul P. and Khemprasit J., *J. Colloid Interface Sci.*, 2006; **297(2)**: 578-583. DOI 10.1016/j.jcis.2005.11.005.
- [19] Ponhan W., Amornkitbamrung V. and Maensiri S., *J. Alloys Compd.*, 2014; **606**: 182-188. DOI 10.1016/j.jcis.2005.11.005.
- [20] Ponhan W., Amornkitbamrung V. and Maensiri S., *Jpn. J. Appl. Phys.*, 2016; **297(2)**: 578-583. DOI 10.7567/JJAP.55.06GJ13.
- [21] Cullity B.D. and Stock S.R., *Elements of X-ray Diffraction*, 3rd Edn., Prentice Hall, Englewood Cliffs, NJ, 2001.
- [22] Sunstrom J.E., Kauzlarich S.M. and Klavins P., *Chem. Mater.*, 1992; **4(2)**: 346-353. DOI 10.1021/cm00020a022.
- [23] Wongsaprom K., *Magnetic Behavior of Dilute Magnetic Oxide Nanoparticles of 3d-Transition Metal doped $La_{0.5}Sr_{0.5}TiO_3$* , PhD Thesis, Khon Kaen University, 2009.
- [24] Wongsaprom K., Venkatesan M., Maensiri S. and Coey J.M.D., *J. Phys. Condens. Matter*, 2010; **22(9)**: 096004(1-9). DOI 10.1088/0953-8984/22/9/096 004.
- [25] Elfimov I.S., Yonoki S. and Sawatzky G.A., *Phys. Rev. Lett.*, 2002; **89(21)**: 216403(1-4). DOI 10.1103/PhysRevLett.89.216403.
- [26] Patterson C.H., *Phys. Rev. B*, 2006; **74(14)**: 144432(1-13). DOI 10.1103/PhysRevB.74.144432.
- [27] Herranz G., Basletic M., Bibes M., Ranchal R., Hamzic A., Tafra E., Bouzehouane K., Jacquet E., Contour J.P., Barthelemy A. and Fert A., *Phys. Rev. B*, 2006; **73**: 064403(1-7). DOI 10.1103/PhysRevB.73.064403.
- [28] Shein I.R. and Ivanovskii A.L., *Phys. Lett. A*, 2007; **371(1-2)**: 155-159. DOI 10.1016/j.physleta.2007.06.013.
- [29] Eliseev E.A., Morozovska A.N., Glinchuk M.D. and Blinc R., *J. Appl. Phys.*, 2011; **109(9)**: 094105(1-5). DOI 10.1063/1.3580478.
- [30] Fang Y., Kuijuan J., HuiBin L., Meng H., Cong W., Juan W. and GuoZhe Y., *Sci. China Phys. Mech. Astron.*, 2009; **53(5)**: 852-855. DOI 10.1007/s11433-010-0187-x.