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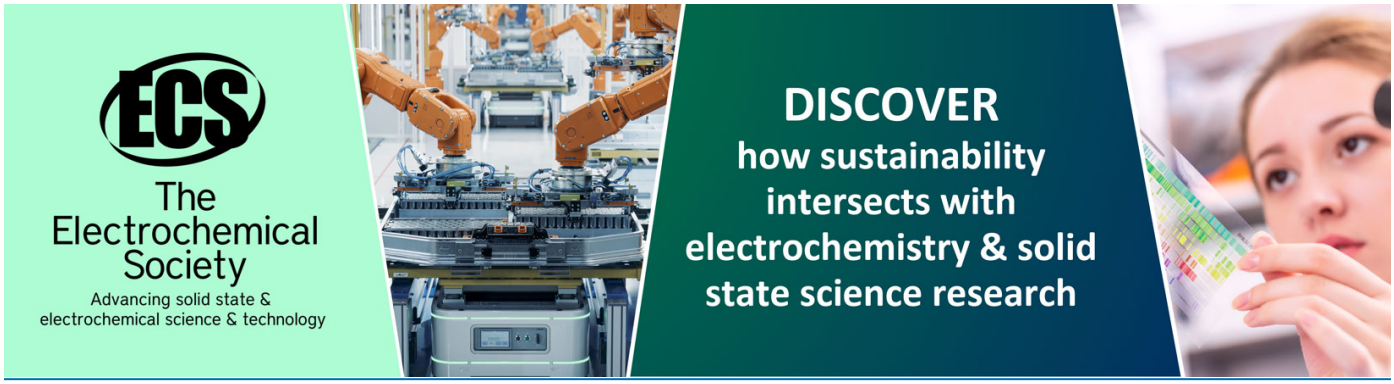

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Characterization of magnetite (Fe_3O_4) minerals from natural iron sand of Bonto Kanang Village Takalar for ink powder (toner) application

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Abstract. This research is about magnetite's characterization (Fe_3O_4) from natural iron sands of Bonto Kanang Village, District of Takalar for ink powder (toner) application. This study aims to determine the process parameters to obtain magnetite of high purity degree and to observe its physical characteristics as a supporting toner material which synthesized through co-precipitation method. The iron sand was first separated by the magnetic technique and dissolved into HCl solution before conducting the precipitation process. Precipitation was done by dripping ammonium hydroxide (NH_4OH). The precipitated powder was dried at 100°C, and then calcined at 400°C. The purity degree and magnetite mineral grain size were analyzed by XRD and SEM-EDS. The EDS elemental test before and after precipitation shown an increase of iron oxide composition from 66.70% to 87.76%. Diffractogram of XRD before and after precipitation showed Fe_3O_4 compounds with magnetite phase of 59% and 98%, respectively. The crystal structure iron sand powder structure before and after precipitation is cubic with each lattice parameters a = b = c = 8.384971 Å, V = 589.528423 Å^3 and a = b = c = 8.386829 Å and V = 589.920291 Å^3 when angle $\alpha = \beta = \gamma = 90^o$. SEM images (using SE and HV 20kV) showed inhomogeneous magnetite morphology. The magnetite phase percentage that obtained based on the XRD analysis gives information that magnetite precipitation has been successfully performed with high degree of purity. The material obtained can be applied as a support toner material.

1. Introduction

South Sulawesi province has the abundance of iron sands as in the District of Takalar [1]. Iron sand deposits contain magnetic minerals such as maghemite (γ-Fe_2O_3) [2], hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) [3]. The content of minerals in the iron sand is very potential as industrial materials. Mineral magnetite can be used as a biomedical application [4], diagnose including MRI (Magnetic Resonance Imaging) [5, 6], cell separation [7], drug delivery system [8-10] antibacterial activity [11], protein separation [12], hyperthermia [13-15], as magnetic catalyst on a magnesium based hydrogen storage material [16], and manufacture of ink powder (toner) [17].

Toner is a composite powder that contains a polymer, pigment, magnetite (Fe_3O_4), and additives which are used for electrophotography printing and photocopying processes. One of the most important ingredients of toner supporters is magnetite minerals because this it acts as a provider the tribocharging property for toner particles [17]. Therefore, the presence of magnetite minerals (Fe_3O_4) is needed as a toner support material.

Various methods have been reported to synthesize Fe_3O_4 among others is chemical reduction [18], sol-gel [19], electrochemical [20], flow injection [21], solvothermal [22], hydrothermal [23], microwave-assisted [24], polyol method [25], co-precipitation [26] etc. In this research, the method that used is co-precipitation method, where the parameters to be optimized are the duration of heating, grinding duration, extraction and calcination process. The use of co-precipitation methods is currently the most widespread concern because the process is simple, easy and cheap [27].

In this research the characterization of micro structure of natural iron sand in Bonto Kanang Village Takalar is done in Microstructure Laboratory of Physics Department of FMIPA UNM by using SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) to know morphology and composition of mineral compound and to know crystal structure, phase of Fe_3O_4 compounds and crystal size through XRD (X-Ray Diffraction) measurement data by using Debye Scherrer analysis.

2. Experimental Method

The main material used in this research is the iron sand of Bonto Kanang Village, Takalar District taken at some point randomly. In the first stages, iron sand was separated by the magnetic technique using a permanent magnet. Subsequently, the sample was crushed for 6 hours then tested using XRD and SEM-EDS methods to examine its the crystal structure, phases, morphological conditions and composition of the compound in the iron sand.

The separation result was weighed by a ratio of 25 grams of iron sand and 150 millilitres of HCl while stirred and heated to a temperature of 100°C using a magnetic stirrer at 350 rpm in 1 hour. Precipitation was done by dripping ammonium hydroxide (NH_4OH), dissolved to pH 6 and forming the precipitated reaction:

$$2FeCl_3 + 3H_2O + 6NH_4OH \longrightarrow 2Fe(OH)_3 + 6NH_4Cl + 3H_2O$$

The precipitated powder washed with H_2O and dried in the memmert oven at 100°C for 19 hours, the reaction:

$$2Fe(OH)_3 + 6NH_4OH + 3H_2O \longrightarrow 2FeOOH + 6NH_4Cl + 5H_2O$$

Furthermore, precipitated powder was calcined at 400°C with heated time for 1 hour.

Characterization was used XRD (X-Ray Diffractometer) Rigaku MiniFlex II method with PDXL2 software to find out the crystal structure, compound phase and crystal size used Deybe Scherrer analysis and SEM-EDS (Scanning Electron Microscopy- Energy Dispersive Spectroscopy) Tescan Vega 3SB to know the morphology and composition of the compound.

3. Results and Discussion

The result of EDS spectrum test of iron sand can be seen in figure 1; these spectrums show the compound composition in the iron sand is an iron oxide especially ferrous oxide (FeO).

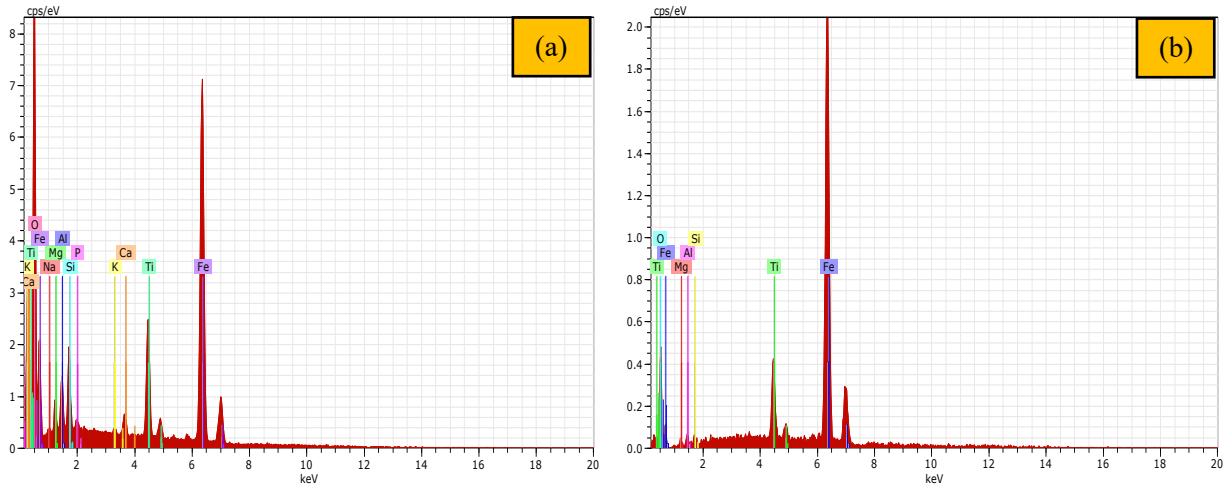

Figure 1. The EDS result of iron sand spectrum test, (a) before precipitation and (b) after precipitation.

Table 1. Result of EDS spectrum before synthesis.

Element	Unn.C [wt.%]	Norm.C [wt.%]	Atom.C [at.%]	Compound norm.C	Comp.C [wt.%]	Error (3 sigma) [wt.%]
Sodium	1.02	1.19	1.57	Na_2O	1.61	0.37
Magnesium	1.85	2.17	2.70	MgO	3.60	0.46
Aluminium	2.38	2.79	3.13	Al_2O_3	5.27	0.48
Silicon	2.40	2.81	3.02	SiO_2	6.01	0.43
Phosphorus	0.31	0.37	0.36	P_2O_5	0.85	0.14
Potassium	0.14	0.16	0.12	K_2O	0.19	0.11
Calcium	0.83	0.97	0.73	CaO	1.36	0.19
Titanium	7.38	8.64	5.46	TiO_2	14.42	0.77
Iron	44.25	51.85	28.05	FeO	66.70	3.73
Oxygen	24.79	29.05	54.87		0.00	9.98
Total	85.34	100.00	100.00			

Table 2. Result of EDS spectrum after synthesis.

Element	Unn.C [wt.%]	Norm.C [wt.%]	Atom.C [at.%]	Compound norm.C	Comp.C [wt.%]	Error (3 sigma) [wt.%]
Titanium	6.20	5.97	4.25	TiO_2	9.95	0.90
Iron	70.92	68.21	41.69	FeO	87.76	6.44
Oxygen	25.56	24.58	52.44		0.00	19.63
Magnesium	0.49	0.47	0.66	MgO	0.78	0.33
Aluminium	0.52	0.50	0.64	Al_2O_3	0.95	0.30
Silicon	0.27	0.26	0.32	SiO_2	0.56	0.20
Total	103.97	100.00	100.00			

The result of EDS analysis above shows the iron oxide compound (FeO) is major compound present in the sample. After synthesis, FeO composition content was higher than before synthesis 66.60% increased to 87.76 wt.%. This result had been accordance with previous studies when iron sand contains the dominant FeO compounds [18]. The impurity compounds present decreased composition content that is TiO2 14.42 wt.% to 9.95 wt.%, SiO2 6.01 wt.% to 0.56 wt.%, Al2O3 5.27 wt.% to 0.95 wt.% .

The presence of iron oxide or ferrous oxide (FeO) compounds in iron sand samples is according to the theory. Because basically iron sand deposits contain iron oxide compounds is magnetic. Also, the formed of Fe_3O_4 compounds expected in this research, that is reaction result between FeO (reduced) and ferric oxide Fe_2O_3 (oxidized) or $FeO + Fe_2O_3 \rightarrow Fe_3O_4$, so the presence FeO is required as the dominant compound in the sample.

Diffractogram of XRD iron sand to present is shown in figure 2. It can be seen that material have dominant composition compound is Fe_3O_4 with magnetite phase. Figure 2 (a) shows the pattern of iron sand diffraction before sample passes through the precipitation stage. XRD analyzed result showed that magnetite phase emerged with composition level 59%, then followed by impurities that Al_2O_3 and CrO_3 respectively 11% and 30%. The crystal structure is cubic with lattice parameters a = b = c = 8.384971 Å where V = 589.528423 $Å^3$ with angle $\alpha = \beta = \gamma = 90^o$. The crystal size was analyzed using Deybe Scherrer equation [28] by taking the highest peak in figure 2 (a). Obtained Fe_3O_4 crystals size before synthesis is 6.39244803 nm.

Figure 2 (b) shows the XRD diffractogram after passing through the precipitation process. From the analyzed results obtained Fe_3O_4 compounds with magnetite phase increased purity from 59% to 98% and ε-Fe_2O_3 impurities 1.7%. The results of the Fe_3O_4 purity study were reported previously by

Zulkarnain et al. 2014 [36], with purity levels obtained 85.80% using mechanical milling method. That means the co-precipitation method performed in this research is far superior compared the mechanical milling method if reviewed based on the purity level. The identification of Fe_3O_4 with high purity levels had been previously reported [18, 25, 31] and the results obtained in this research is close to perfect purity.

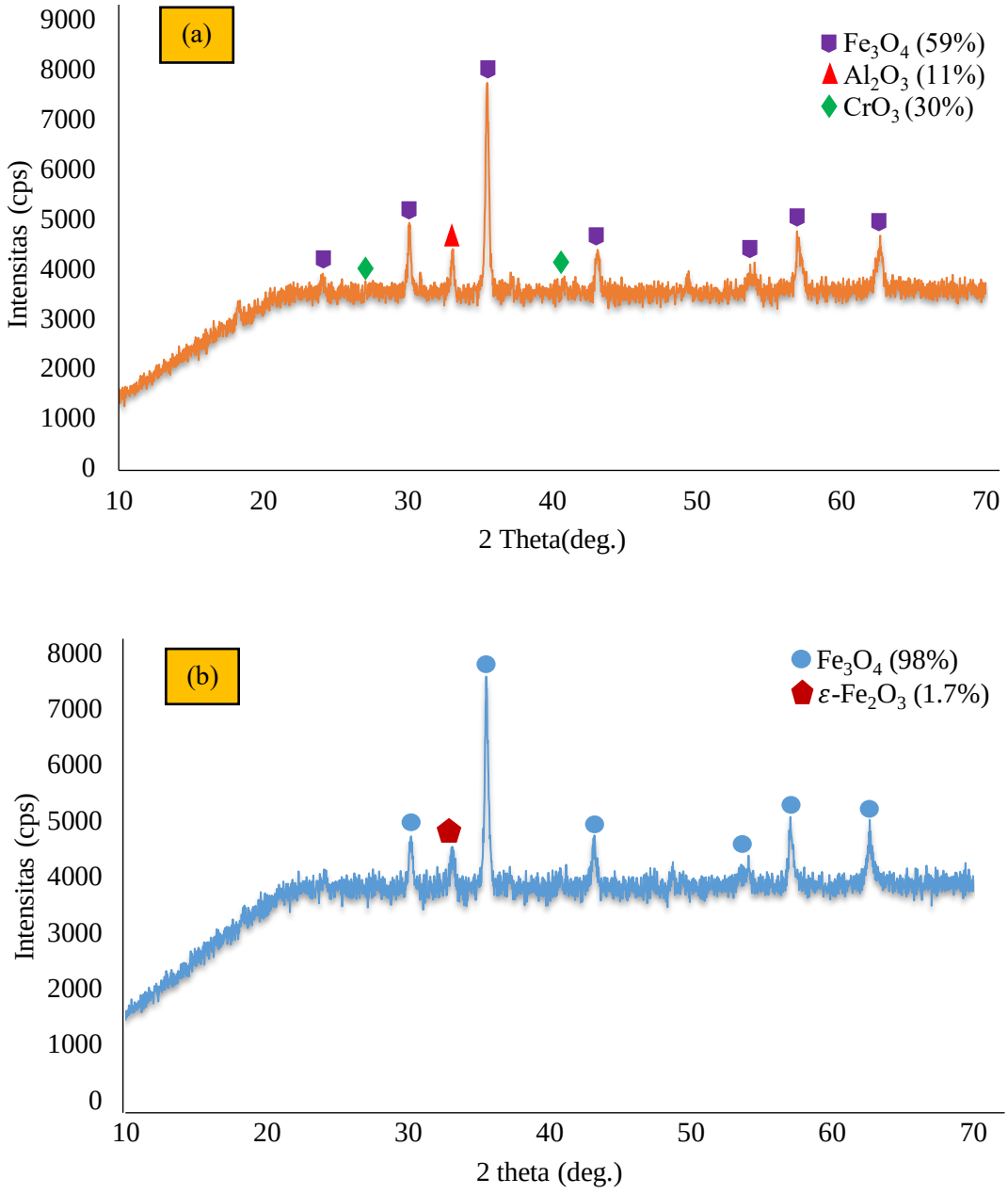

Figure 2. Diffractogram XRD from mineral Fe_3O_4 (a) before precipitation and (b) after precipitation.

The crystal structure sample after precipitation is cubic with lattice parameters a = b = c = 8.386829 Å and V = 589.920291 Å^3 with angle $\alpha = \beta = \gamma = 90^o$. The parameters obtained were similar with research result by Chaki et al, 2015, Setiadi et al, 2016, Puspitaningrum et al, 2017 [18, 29, 30]. The

maximum intensity value was obtained is I (cps) = 7120 at bragg angle $2\theta = 35.497^{o}$, which is reflected at the maximum peak (311) [10, 31-35] and corresponds to (JCPDS card No. 19-629) [37, 38].

The crystal size Fe_3O_4 was obtained based on Debye Scherrer analysis [39]. The results of the analysis obtained in this study was appropriate with previous research [18] where the crystal size obtained was 7.20 nm. In this research, the magnetite crystal size of natural iron sand of Bonto Kanang Village Takalar was found 5.57994062 nm.

SEM investigations were conducted to identify the morphological conditions and homogeneity of the iron sand sample. SEM images of the Fe_3O_4 mineral is shows in figure 3.

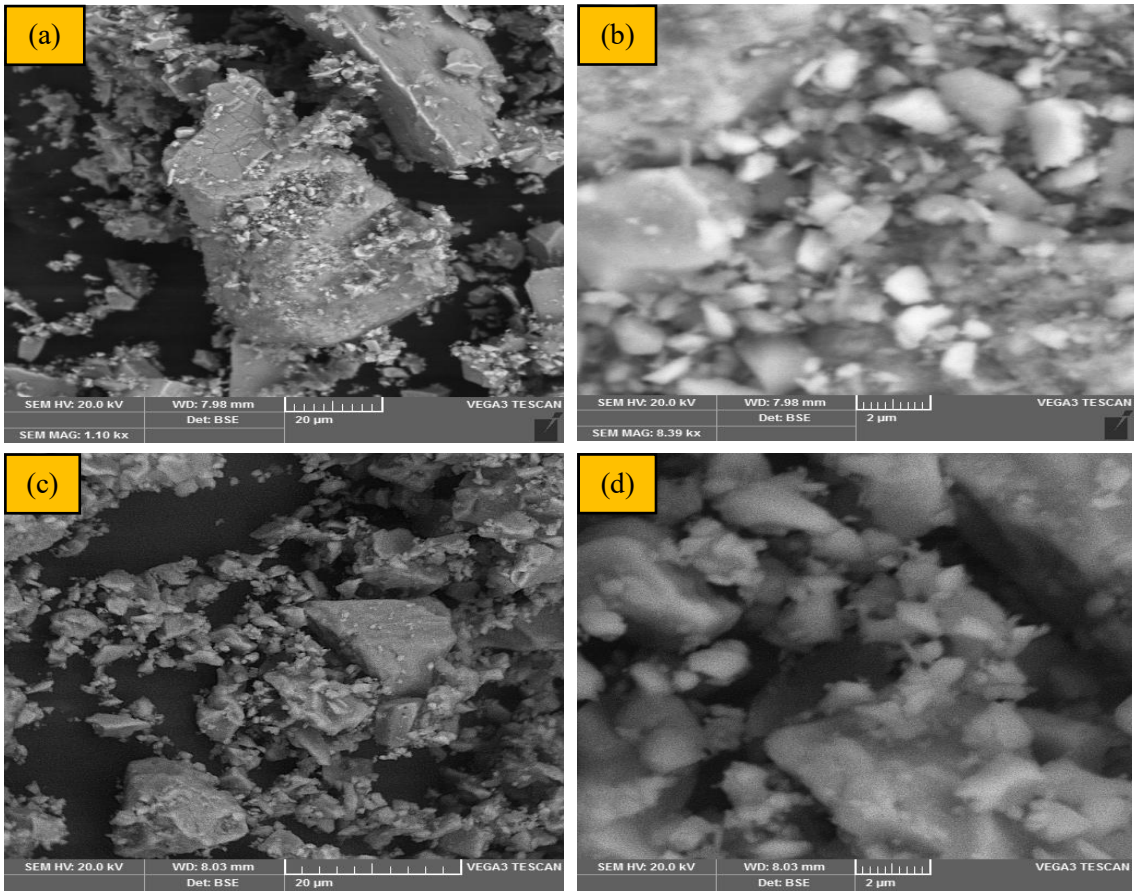

Figure 3. Morphology of iron sand (a, b) before precipitation and (c, d) after precipitation.

Figure 3 (a), (b) and (c), (d) each shows the morphological condition of iron powder before and after precipitation at 20 μm and 2 μm respectively. Based on SEM image using SE and HV detector 20 kV, it is seen that morphological conditions of iron sand appeared inhomogenous because of clumps. These visible clump is an agglomeration of tiny particles formed by scouring and calcination processes.

4. Conclusions

Characterization of mineral magnetite of natural iron sand of Bonto Kanang Village Takalar was successfully by co-precipitation method. The results of this study indicated that based on EDS spectrum analysis the composition content of FeO compound increased from 66.70 wt.% to 87.76 wt.%. While the result of XRD diffractogram before and after precipitation showed that iron sand successfully obtained high purity level from 59% to 98%. The purity level obtained is greatly influenced by the process parameters which is conducted in the research that is optimization during the precipitation process, drying the precipitation result at 100^{o}C for 19 hours, and the optimum calcination time is 1 hour

where the calcination temperature is constant 400°C. The results obtained from this research has been accordance with the results of research previously reported and can be applied as a support toner.

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References
[1] Aly S H and Takdir T 2011 *J. Transportasi* **11** 123
[2] Jarzebski M, Kościński M and Białopiotrowicz T 2017 *Journal of Physics*: *Conf. Series* **885**-012007.
[3] Kurniawan C, Eko A S, Ayu Y S, Sihite P T A, Ginting M, Simamora P and Sebayang P 2017 *Mater. Sci. Eng: Conf. Series* **202** 012051
[4] Mishra A 2014 *Int. J. Mech. Eng. Robot.* **3** 410
[5] Phillips M A, Gran M L and Peppas N A 2010 Targeted nano delivery of drugs and diagnostics, nano today, tom 5, p. 143 – 159
[6] Lee J H, Jun Y W, Yeon S I, Shin J S and Cheon J 2006 *Angew. Chem. Int. Edn* **45** 8160-2
[7] Jing Y et al 2007 *Biotechnol. Bioeng*. **96** 1139–54
[8] Neuberger T, Schöpf B, Hofmann H, Hofmann M and Von Rechenberg B 2005 *J.Magn. Magn. Mater*. **293** 483–96
[9] Bucak S, Yavuztürk B and Sezer A D 2012 *Recent Advances in Novel Drug Carrier Systems* ed A D Sezer (Rijeka: InTech)
[10] Xuan N P, Tan P, Tuyet N P, Thi T N T and Thi V T T 2016 *Adv. Nat. Sci.: Nanosci. Nanotechnol*. **7** 045010
[11] Inbaraj B S, Tsai T-Y and Chen B-H 2012 *Sci. Technol. Adv. Mater*. **13** 015002
[12] Gu H, Xu K, Xu C and Xu B 2006 *Chem. Commun*. **9** 941
[13] Ito A et al. 2003 *Cancer Sci*. **94** 308
[14] Spiers K, Cashion J and Gross K 2003 *Key Eng. Mater. Bioceram.* **213** 254
[15] Múzquiz-Ramos E M, Guerrero-Chávez V, Macías-Martínez B I, López-Badillo C M and García-Cerda L A 2015 *Ceram. Int.* **41** 397
[16] Huang Z G, Guo Z P, Calka A, Wexler D, Lukey C dan Liu H K 2006 *J. Alloy. Compd.* **422**
[17] Ataeefard M, Ghasemi E and Ebadi M 2014 *Sci. World J.* **2014** 706367
[18] Chaki S H, Tasmira J M, Chaudhary M D, Tailor J P and Deshpande M P 2015 *Adv. Nat. Sci: Nanotechnol.* **6** 035009
[19] Xu J, Yang H, Fu W, Du K, Sui Y, Chen J, Zeng Y, Li M and Zou G 2007 *J. Magn. Magn. Mater*. **309** 307
[20] Cabrera L, Gutierrez S, Menendez N, Morales P and Herrasti P 2008 *Electrochim. Acta*. **53** 3436
[21] Alvarez S, Muhammed M and Zagorodni A 2006 *Chem. Eng. Sci*. **61** 4625
[22] Liu M and Kim K 2009 *Mater. Lett*. **63** 428
[23] Zhang J, Chen Y, Wang N and Shi W 2008 *J. Cryst. Growth* **310** 5453
[24] Hong Y, Pan T and Li Z 2006 *J. Magn. Magn. Mater*. **303** 60
[25] Vega-Chacón J, Picasso G, Avilés-Félix L and Jafelicci J M 2016 *Adv. Nat.: Nanotechnol.* **7** 015014
[26] Venkatesan M, Nawka S, Pillai S and Coey D 2003 *J. Appl. Phys*. **93** 8023
[27] Shen L, Qiao Y, Guo Y, Tan J 2012 Tianjin University **39** 737
[28] Mai T T T, Le P T H, Pham H N, Do H M and Phuc X 2014 *Adv. Nat. Sci: Nanosci. Nanotehnol.* **5** 045007
[29] Setiadi E A, Sebayang P, Ginting M, Sari A Y, Kurniawan C, Saragih C S and Simamora P 2016 *J. Phys: Conf. Series* **776** 012020

[30] Puspitaningrum A, Taufiq A, Hidayat A, Sunaryono, Hidayat N and Samian 2017 *Materials Science and Engineering: Conf. Series* **202** 012054
[31] Cuenca J A, Bugler K, Taylor S, Morgan D, Williams P, Bauer J and Porch A 2016 *J. Phys: Condens. Matter* **28** 106002
[32] Fahmiati, Nuryono and Suyanta 2017 *Materials Science and Engineering: Conf. Series* **172** 012020
[33] Guan B, Ding D, LeFan W J and Xiong R 2017 *Mater. Res. Express* **4** 056103
[34] Kurniawan C, Eko A S, Ayu Y S, Sihite P T A, Ginting M, Simamora P and Sebayang P 2017 *Materials Science and Engineering: Conf. Series* **202** 012051
[35] Yusmaniar, Adi W A, Taryana Y, Muzaki R 2017 *Materials Science and Engineering: Conf. Series* **196** 012033
[36] Jalil Z, Sari E N, Ismail A B and Handoko E 2014 *Indones. J. Appl. Phys.* **4** 1
[37] Rahmawati R, Melati A, Taufiq A, Sunaryono, Diantoro M, Yuliarto B, Suyatman S, Nugraha N and Kurniadi D 2017 *Materials Science and Engineering: Conf. Series* **202** 012013
[38] Khashan, Dagher S, Omari S A and Tit N *Mater. Res. Express* **4** 055701
[39] Chaki S, Deshpande M, Chaudhary M and Mahato K 2013 *Adv. Sci. Eng. Med.* **5** 285