Jusami Jurnal Sains Materi Indonesia
Homepage: http://jusami.batan.go.id
Akreditation No : 21/E/KPT/2018
Date 9 July 2018
ISSN 1411-1098
E-ISSN 2614-087X

THE EFFECT OF CALCINATION ON MICROWAVE ABSORBING PROPERTIES OF Fe_3O_4/TiO_2 COMPOSITE

Adel Fisli[1], Didin S. Winatapura[1], Wisnu Ari Adi[1], Yana Taryana[2]

[1]Center for Science and Technology of Advanced Materials- National Nuclear Energy Agency, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten, Indonesia

[2]Research Center for Electronics and Telecommunication, Indonesian Institute of Sciences, Bandung, West Java, Indonesia

Email: adel@batan.go.id

Received: 10 September 2018 *Revised: 11 December 2018* *Accepted: 18 December 2018*

ABSTRACT

THE EFFECT OF CALCINATION ON MICROWAVE ABSORBING PROPERTIES OF Fe_3O_4/TiO_2 COMPOSITE. The Fe_3O_4/TiO_2 composites have been fabricated by simple precipitation method for microwave absorbing. The obtained powder of Fe_3O_4/TiO_2 which 10 % iron oxide containing were calcinated from 300^{o}C – 700^{o}C for 3 hours. The characteristic of samples was investigated by various techniques. The TEM image showed the composites form agglomeration with particles size of around 20 nm. The all sample contents most of the anatase phase. The increasing of calcination temperature is the bigger of crystallite size. The Raman bands shift towards lower wavenumber and their full-widths at half-maximum (FWHM) of the bands decreases as the particles size increase. The measurement of the magnetic properties illustrated that the Fe_3O_4/TiO_2 exhibited paramagnetic behavior at room temperature. The microwave absorbing properties of the sample was measured by VNA using frequency microwave filter in X-band range (8-12 GHz). The reflection loss (RL) values were calculated for thickness 1 mm of the sample. The minimum reflectivity peak value tends to decrease with the increase of the calcination temperature due to increasing the crystallite size of the particles. The lowest reflectivity value of Fe_3O_4/TiO_2 was occurred calcinated at 600^{o}C with -13.4 dB loss at 10.9 GHz, that is more 80% absorbed of the electromagnetic wave in thickness 1 mm of the sample. The microwave absorption properties the calcinated 700^{o}C the sample decrease due to the loss of magnetic properties of the sample. This study concluded that increase in average crystalline size, microwave absorption properties increased. However, the decrease drastically of magnetic properties of the sample causes microwave absorption properties to decrease.

Keywords: RAM (radar absorbing material), composite, titanium, magnetite, calcination effect.

ABSTRAK

PENGARUH KALSINASI TERHADAP SIFAT SERAPAN GELOMBANG MIKRO KOMPOSIT Fe_3O_4/TiO_2. Komposit Fe_3O_4 /TiO_2 telah berhasil dibuat dengan metode presipitasi sederhana untuk menyerap gelombang mikro. Serbuk Fe_3O_4/TiO_2 yang diperoleh (mengandung 10% oksida besi) dikalsinasi dari suhu 300^{o}C - 700^{o}C selama 3 jam. Karakteristik sampel diselidiki dengan berbagai teknik. Foto *TEM* menunjukkan bahwa komposit membentuk aglomerasi dengan ukuran partikel sekitar 20 nm. Semua sampel mengandung fase anatase. Semakin meningkat suhu kalsinasi maka ukuran kristalin juga meningkat. Pita Raman bergeser ke arah bilangan gelombang rendah dan juga *full-widths at half-maximum* (FWHM) semakin sempit menandakan ukuran kristalin meningkat dengan meningkatnya suhu. Komposit Fe_3O_4 /TiO_2 memperlihatkan perilaku paramagnetik pada suhu kamar. Sifat serapan gelombang mikro sampel diukur dengan alat VNA dalam rentang frekuensi gelombang X-band (8-12 GHz) pada ketebalan sampel 1 mm. Nilai *reflection loss* (R_F) cenderung menurun dengan meningkatnya suhu kalsinasi karena meningkatnya ukuran kristal partikel. Nilai *reflection loss* terendah (terbaik) terjadi pada suhu kalsinasi 600^{o}C dengan -13,4 dB pada frekuensi 10,9 GHz, artinya lebih 80% gelombang elektromagnetik diserap pada ketebalan sampel 1 mm. Sifat serapan gelombang mikro pada 700^{o}C berkurang karena hilangnya sifat magnetik bahan. Studi ini disimpulkan bahwa semakin besar ukuran kristal maka sifat serapan gelombang mikro bahan juga meningkat. Namun demikian, penurunan dratis sifat magnetik bahan menyebabkan sifat serapan gelombang mikro sampel juga menurun.

Kata kunci: RAM (Radar Absorbing Material), Komposit, Titanium, Magnetite, Efek kalsinasi

INTRODUCTION

A radar-absorbing material (RAM) diminishes the stage of electromagnetic energy reflected, or scattered, from its surface [1]. It has been applied as in equipment electromagnetic shielding employed in automotive and aerospace industries, military technology, electrical and electronic devices and systems for wireless communication [2]. The excellent of radar absorbing material (RAM) should have high absorption, broadband and intend light quality performance [3]. The materials are classified into two types, according to their interactions with the electromagnetic wave: materials with dielectric losses, which interact with the electric wave field, and materials with magnetic losses, which interact with the wave magnetic field. Therefore, the dielectric and magnetic materials are the focus of extensive study for microwave absorbers [2].

The absorption behavior of electromagnetic-absorber interaction mainly depends on the dielectric properties of the absorber and the amount of absorption which can be expressed by reflection loss (RL). The value of RL is defined as:

$$RL = -20log\left|\frac{Z_{in}-Z_o}{Z_{in}-Z_o}\right| \quad (1)$$

where Z_{in} is the impedance of absorbing materials and Zo is the impedance of free space. The impedance of absorbing material (Zin) depended on the complex permittivity and complex permeability of the absorbing material and defined as:

$$Z_{in} = Z_o\sqrt{\left(\frac{\mu_r}{\varepsilon_r}\right)}\, tanh\left\{j\left(\frac{2\pi fd}{c}\right).\sqrt{(\mu_r\varepsilon_r)}\right\} \quad (2)$$

where μr and εr are the complex permeability and permittivity of the composite materials, f is the working frequency, d is the thickness of the microwave absorber, and c is the velocity of light. Base on equations 1 and 2 that the value of RL depends on the complex permittivity, complex permeability, thickness of absorber and working frequency [4].

Titania is known to apply to a range of beneficial technological areas as a white pigment in the various material industry and photocatalyst [5]. The titanium oxide TiO_2 as the stable dielectric material is also useful material for electromagnetic wave absorption. Few articles concerning the microwave absorbing properties of TiO_2-based composites have been reported such as titanium oxide and rubber composite [6] doped barium hexaferrite/TiO_2/ conducting carbon black [7], chlorinated polyethylene/ TiO_2 [8] $MnFe_2O_4/TiO_2$ nanocomposite [9], metal dispersed TiO_2 nanocomposite [10]. The composite of TiO_2 and iron oxide is a better match for the dielectric loss, and magnetic loss may be realized. Zhu et al. (2010) [11] reported that Fe_3O_4/TiO_2 core/shell nanotubes for electromagnetic wave absorption were fabricated through a three-step process, e.i. Hydrothermal method, a wet-chemical method and calcination process under a mixture of Ar/H_2 flow. The maximum reflection loss of the material reaches -20.6 dB at 17.28 GHz for the absorber with a thickness of 5 mm.

Beside of the material composition, The morphology and particles size play very important role in absorbing behavior. The increasing of crystalline size does shift not only the position of reflection loss toward higher frequency region but also lower the minimum reflection loss [12]. The calcination can strongly affect on the particles size, morphology and magnetic properties [13]. Kumar et al.,(2013) [14] reported that the particles size had significant influence on the dielectric and absorption properties of the material. The complex dielectric properties, loss targets, reflection loss and bandwidth increase with the increase in average particles size.

Previous work, the effect of Fe^{2+} and Fe^{3+} substitution on the crystal structure, optical and magnetic properties of anatase $Ti_{1-\delta}(\delta\%Fe^{2+})O_2$ nanoparticles at 500^{o}C in calcinations temperature has been studied. Up to 5% of either Fe^{2+} or Fe^{3+} successfully substituted into Ti^{4+} without changing the crystal structure of titania [15]. The effect of particles size on microwave absorption is very less attention in the literature. The particles size value and particles morphology are depended at calcination step. Therefore, this paper is intended as an investigation of preparation of the titania-magnetite by simple precipitation method. They were grown in size by increasing the calcination temperature step at 300, 400, 500, 600 and 700^{o}C under atmosphere condition. The investigated materials are discussed includes; morphology, phase and crystallite size analysis, chemical bonding, magnetic properties and microwave absorption properties at X-band.

EXPERIMENTAL METHOD

Materials

Chemical including Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), Titanium tetrachloride ($TiCl_4$) 98%, Ammonia 25%, Hydrochloride (HCl) were analytical grade (Merck) and were used without further purification.

Preparation of TiO_2/Fe_3O_4

The solution of 0.3M $TiCl_4$ was prepared from Titanium tetrachloride ($TiCl_4$) 98% in distilled water in an ice-water bath. In another container, 5.2 g of $FeCl_3.6H_2O$ and 2.0 g of $FeCl_2$ were dissolved in 10 mL HCl 1 N under vigorous stirring and continued to add 15 mL distilled water. This mixture results in an aqueous solution with a molar ratio of Fe(II)/Fe(II)= 0.5. It is important to perform the Fe_3O_4 produce. The iron salts were mixed with $TiCl_4$ solution under vigorous stirring at room temperature. The resulting solution was added drop into 250 mL of 1.5 NH_4OH solutions under vigorous stirring. The formed precipitate was isolated from supernatant by decantation process. Obtained solid was repeatedly washed until the pH solution of supernatant was neutral. The solid was dried in oven at 100°C, further calcinated in furnace under atmosphere at 300°C, 400°C, 500°C, 600°C and 700°C for 3 hours.

Characterization

XRD patterns of the samples were recorded on an Empyrean Panalytical with Cu-Kα radiation, λ=1.154Å operation at 40 kV and 30 mA for the 2θ range 10-80 with scan steps of 0.02. The average crystallite size according to the Debye-Scherrer formula using XRD data. The magnetic properties were measured by vibrating sample magnetometer (VSM-Oxford type 1.2 T) at room temperature in the applied field rate 0.25 Tesla/minute, range from -1 to +1 Tesla. The morphology of the composite was examined by transmission electron microscopy (TEM, JEM-14000 JOEL). TEM sample was prepared by dispersing the sample in ethanol and dropping the suspension on a copper grid. Raman spectra were observed by a Raman spectrometer Bruker serial number 254 at radiation of 785 nm the power 1 mW. The microwave absorption properties of the composite were calculated at room temperature using a microwave vector network analyzer (VNA-ADVANTEST R3770) with a frequency range from 8 to 12 GHz.

RESULTS AND DISCUSSION

Figure 1 shows the transmission electron microscopy (TEM) image of TiO_2/Fe_3O_4 at 500°C calcination. It can clearly see that TiO_2/Fe_3O_4 particles are spherical form. It is obvious from this image that the TiO_2/Fe_3O_4 particles are dispersed with around particle size of 20 nm with agglomeration form. The particles size of samples from the TEM images are in good agreement with the value obtained by applying the Scherrer equation to the XRD patterns.

Figure 2 show XRD patterns for calcinated variant of TiO_2/Fe_3O_4 powder from 300°C to 700°C. The peaks appear at 2θ = 25.4°; 37.9°; 48.1°; 53.4o; 55.9°; 62.8°; and 75.1°. All peaks are agreement with the standard spectrum JCPDS no. 21-1272) which are well indexed to the anatase phase (101), (004), (200), (105), (211), (118), and (220), respectively. Especially, for calcinated 700°C of the sample appeared the new diffraction at 27.24° and 32.36° which are denoted to rutile and illmenite phase, respectively. Hanaor et al. (2011) [5] reported that the anatase to rutile transformation is not immediately which it need time for reconstruction. The pure bulk anatase is considered widely begin to transform irreversibly to rutile in air at 600°C. Actually, the transition temperature can occur in the range 400-1200°C. The average crystallite diameter (ACD) of the TiO_2 particles was determined from the major diffraction peak (101) using the well-known Scherrer's formula.

$$ACD = \frac{K\lambda}{\beta cos\theta} \quad (3)$$

where K is the Scherrer constant, λ is the X-ray wavelength, θ is the angle of Bragg diffraction, and β is the difference between the full-width at half-maximum (FWHM) which has been corrected by the instrumental broadening. The average particles sizes observed at different sintering conditions are given in Table 1. The calculated ACD value of nanocrystalline TiO_2/Fe_3O_4 variation is found in range 7.25 - 30.14 nm. This value is in agreement with the result of TEM investigation. The increasing of calcination temperature is the bigger of crystallite size. The results indicate that the particles size growth under the influence of sintering. Evidently, the sintering temperature promotes enlargement of grain boundaries and consequently particles size increases as a function of sintering temperature.

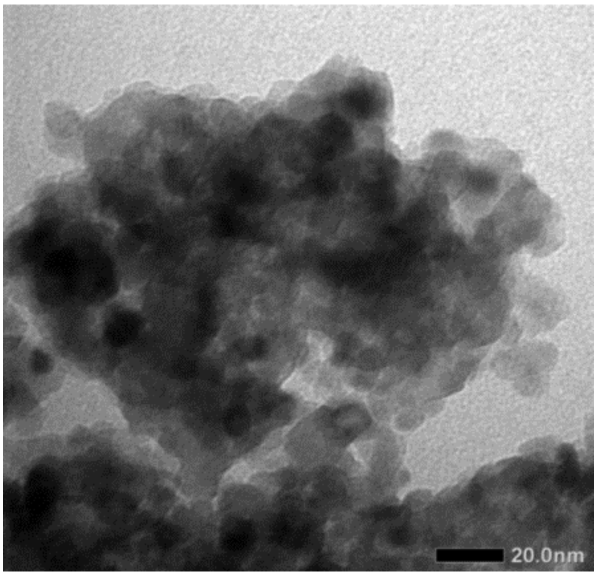

Figure 1. TEM images of TiO_2/Fe_3O_4 powder at 500°C calcinations, representative.

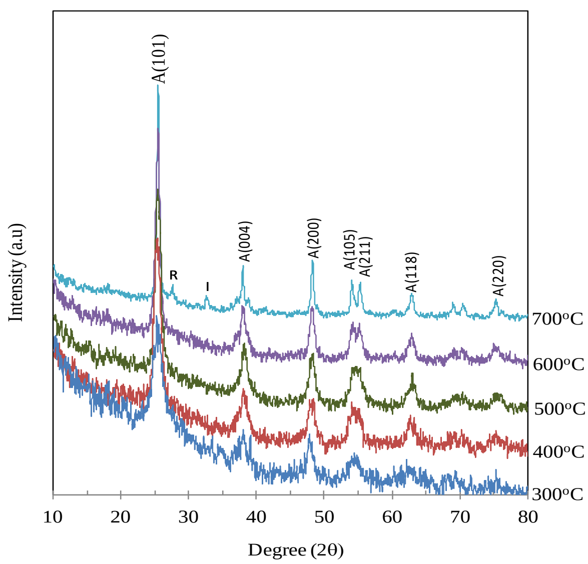

Figure 2. XRD pattern of Fe_3O_4/TiO_2 powder annealed from 300°C to 700°C for 3 hours, A=anatase, R=Rutile, and I=Ilmenite

Table 1. The crystalline size and E_g Raman active modes values for annealed samples

No	Calcination temperature	Crystalline size (nm)	E_g Raman active modes (cm^{-1}) FWHM	Center E_g
1	300°C	7.25	25.24	151
2	400°C	9.59	18.99	147
3	500°C	10.77	16.71	146
4	600°C	14.63	14.76	145
5	700°C	30.14	12.91	144

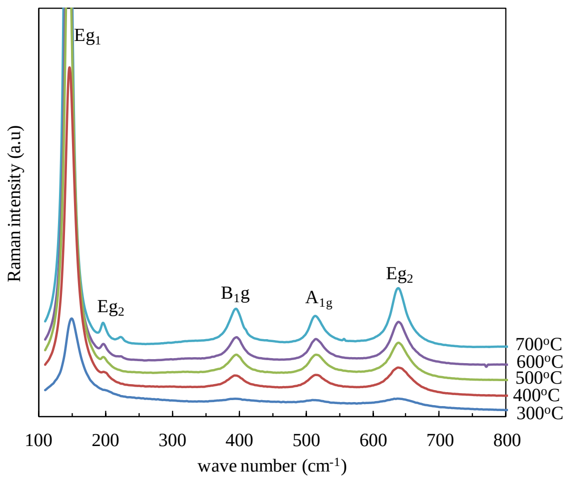

Figure 3. Raman spectra of Fe_3O_4/TiO_2 powder annealed from 300°C to 700°C for 3 hours.

TiO_2 nanoparticles have frequently been investigated with Raman spectroscopy. Based on the space group D4h for anatase and assumed site symmetries for the TiO and O atoms within the unit cell (D_2d for Ti; C_2v for O) shows six Raman active modes (A_1g, $2B_1g$, and 3Eg). Osaka has explained that the Raman spectrum of an anatase single has six modes such as at 144 cm^{-1} (Eg), 197 cm^{-1} (Eg), 399 cm^{-1} (B_1g), 513 cm^{-1} (A1g), 519 cm^{-1}, and 639 cm^{-1} (Eg) [16]. The observed Raman bands at 639 cm^{-1}, 519 cm^{-1}, and 399 cm^{-1} are consistent with the moderately distorted TiO_6^{8-} octahedron in anatase. The sharp peaks at 197 cm^{-1} and 144 cm^{-1} are consistent with Ti-Ti bonding present at the octahedral chains [17]. In this study in Figure 3, the obtained Raman bands of varied samples are in the range of 151-144 cm^{-1} (Eg), 196-197 cm^{-1} (Eg), 394-396 cm^{-1} (B1g), 510-515 cm^{-1} (A1g), and 637- 639 cm^{-1}(Eg). Based on analysis of the Raman band, we declare that the sample has anatase for all samples. The results agree with obtained XRD analysis. The change of TiO2 particles size can be known with studying of band broadening and shifts of Raman bands. It is clear seen that the Raman bands shift towards lower wavenumber and their full-widths at half-maximum (FWHM) of the bands decreases as the particles size increase (insert Figure 3). The Raman shifts are due to the effects of alteration of particles size on the force constants and vibrational amplitudes of the nearest neighbor bonds. While the broadening of Raman bands increases with decreasing particles size. This broadening of the phonon momentum leads to broadening of the scattered phonon momentum [16].

The measured magnetic properties of Fe_3O_4/TiO_2 samples annealed at different temperatures are shown in Figure 4. The measurement of the magnetic properties by VSM attributed that the Fe_3O_4/TiO_2 exhibited paramagnetic behavior at room temperature. Inser Figure 4 shown the saturation magnetization versus calcination temperature of the samples. The sample was annealed from 100°C to 300°C shows that the saturation magnetization of sample increase with increasing of annealing temperature. However, further increasing of annealed temperature from 300°C to 600°C is occurred decreases gradually the saturation magnetization (Ms) value of the sample. The loss of Ms can be attributed to the transformation phase of iron oxide partially from magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3) [18]. Finally, saturation magnetization of the sample decreases drastically for annealing temperature of 700°C. It can be assigned that maghemite (γ-Fe_2O_3) undergoes phase transition into hematite (α-Fe_2O_3).

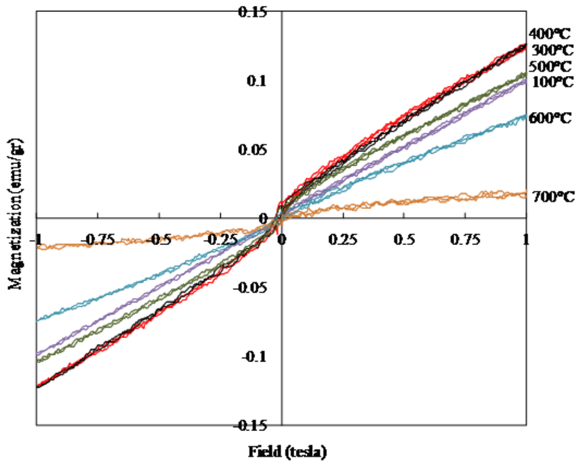

Figure 4. The saturation magnetization of Fe_3O_4/TiO_2 powder annealed from 100°C to 700°C for 3 hours

The reflection loss of the samples in the X band range (8-12 GHz) was shown in Figure 5. The thickness of sample for reflection loss (RF) measurement was about 1 mm. The dips in the values of RL versus frequency imply low reflectivity (and good absorption). As we can see, the minimum reflectivity peak value tends to decrease with the increase of the annealing temperature from 300°C to 600°C. It means that the absorption of electromagnetic wave increases with increasing annealing temperature. It due to increasing the particle size with increasing of annealing temperature, resulting in large dense particles (agglomerates). These results are in line with those reported by Costa et al. (2009) [19] that raising the calcination temperature increased the particle sizes of the powder, improving the reflectivity of the materials. The lowest value of reflection loss was obtained for annealed 600°C with RF -13,4 at 10.9 GHz. These results denoted that more 80%

of electromagnetic wave absorbed on the sample. However, further reflection loss increases with annealed temperature at 700°C. It is due to the decreasing magnetic properties of the material. Magnetic properties such as coercivity (Hc) and saturation magnetization (Ms) can be improved when the grain size is reduced to nanoscale. Thus, the overall microwave absorption is a competition among dielectric properties, magnetic properties and structure of particles (grain/particles size and shape).

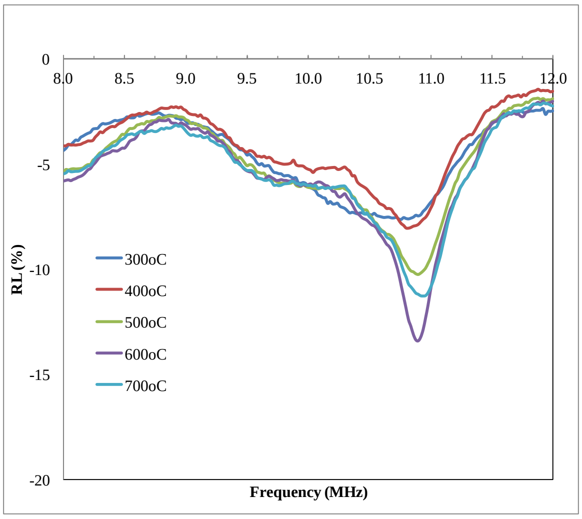

Figure 5. VNA measurement of Fe_3O_4/TiO_2 powder annealed from 300°C to 700°C for 3 hours

CONCLUSIONS

The Fe_3O_4/TiO_2 composite powder with different calcinated temperature has been successfully synthesized by simple precipitation method. The calcination temperature affects on the average crystallite size dan magnetic properties, which plays an important role in absorption of electromagnetic wave. Crystalline size increase and saturation decrease with increasing calcination temperature. Absorption of electromagnetic wave tends to increase with increasing crystallite size. However, the loss of magnetic properties of the sample will decrease the absorption of electromagnetic wave. The minimum RL value of -13,4 dB is observed at 10.9 GHz for calcinated 600°C of the sample with thickness of 1.00 mm.

ACKNOWLEDGMENT

The authors are grateful for the support from Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency, Government Research of the Republic of Indonesia. Financial support by Research and Development of Smart Magnetic Programs for DIPA 2016 grand is gratefully acknowledged.

REFERENCES

[1]. A. Tennant. “Radar-absorbing Materials”, University of Sheffield, UK, 2014.

[2]. V. L. Soethe, E. L. Nohara, L. C. Fontana, M. C. Rezende, “Radar absorbing materials based on titanium thin film obtained by sputtering technique”, *Journal of Aerospace Technology and Management*, vol. 3 no. (3), pp. 279–286, 201.

[3]. H. Chongkang, P. Shunkang, C. Lichun, L. Xing, W. Yajun, “Effect of rare earth on microwave absorbing properties of RE-Co alloys”, *Journal of Rare Earths*, vol. 33, no. 3), pp. 271–277, 2015.

[4]. V. L. Soethe, E. L. Nohara, L. C. Fontana, M. C. Rezende, “Radar absorbing materials based on titanium thin film obtained by sputtering technique”, *Journal of Aerospace Technology and Management*, vol. 3, no. 3, pp. 279–286, 2011.

[5]. H. Hajimiri, M. S. S. Dorraji, M. H. Rasoulifard, A. R. Amani-Ghadim, M. R. Khoshroo, “Combination of perovskite and magnetic inverse spinel structures to improve microwave absorption properties”, *Materials Science and Engineering B*, vol. 225, pp. 75-85, 2017.

[6]. D. A. H. Hanaor, C. C. Sorrell, “Review of the anatase to rutile phase transformation”. *Journal Materilas Science*, vol. 46, pp. 855–874, 2011.

[7]. Y. J. An, H. Okino, T. Yamamoto, S. Ueda, T. Deguchi, “Microwave dielectric properties of lossy dielectric composite material”, *Japanese Journal of Applied Physics*, vol. 45, no. 9B, 2006.

[8]. C. M. Choi, K. S. Ko, “A study on absorption properties of the EM wave absorber using TiO_2 in W-Band”. *Journal of Navigation and Port Research International Edition*, vol. 34, no 2, pp. 111-115, 2010.

[9]. H. M. Xiao, X. M. Liu, S. Y. Fu, “Synthesis, magntic and microwave absorbing properties of core-shell structured $MnFe_2O_4/TiO_2$ nanocomposites”. *Composites Science and Technology*, vol. 66, pp. 2003–2006, 2006.

[10]. A. Kumar, V. Agarwala, D. Singh, “Microwave absorbing behavior of metal dispersed TiO_2 nanocomposites”, *Advanced Power Technology*, vol. 25, pp. 483–489, 2014.

[11]. C. L. Zhu, M. L. Zhang, Y. J. Qiao, G. Xiao, F. Zhang, Y. J. Chen, “Fe_3O_4/TiO_2 core/shell nanotubes: synthesis and magnetic and electromagnetic wave absorption characteritics”, *Journal of Physic Chemistry C*, vol. 114, pp. 16229-16235, 2010.

[12]. Y. Wang, T. Li, L. Zhao, Z. Hu, Y. Gu, “Research progress on nanostructure radar absorbing material”, *Energy and Power Engineering*, vol. 3, pp. 580-584, 2011.

[13]. Y. Qu, H. Yang, N. Yang, Y. Fan, H. Zhu, G. Zou, “The effect of reaction temperature on the particle size, structure and magnetic properties of coprecipitated $CoFe_2O_4$ nanoparticles”, *Materials Letters*, vol. 60, pp. 3548–3552, 2006.

[14]. A. Kumar, V. Agarwala, D. Singh, “Effect of particles size of $BaFe_{12}O_{19}$ on the microwave

absorption characteristics in X-band", *Progress in Electromagnetic Research M*, vol. 29, pp. 223-236, 2013.
[15]. W. A. Adi, A. Fisli, "Efek substitusi Fe^{2+} dan Fe^{3+} terhadap struktur Kristal, sifat optik dan magnetik pada nanopartikel anatase $Ti_{1-\delta}(\delta\%Fe^{2+})O_2$", *Jurnal Sains Materi Indonesia*, Vol. 19 No 2, pp. 54-60, 2018.
[16]. H. C. Choi, Y. M. Jung, S. B. Kim, "Size effect in the Raman spectra of TiO2 nanoparticles", *Vibrational Spectroscopy*, vol. 37, pp. 33-38, 2005.
[17]. F. D. Hardcastle, "Raman spectroscopy of titania (TiO_2) nanotubular water-splitting catalysts", *Journal of the Arkansas Academy of Science*, vol. 65, pp. 43-48, 2011.
[18]. A. Sutka, S. Lagzdina, T. Kambre, P. Parna, V. Kisand, J. Kleperis, M. Maiorov, A. Kikas, I. Kuusik, D. Jakovlevs, "Study of the structure phase transformation of iron oxide nanoparticles from an Fe^{2+} ion source by precipitation under various synthesis parameter and temperature". *Materials Chemistry and Physic*, vol. 149, pp. 473–479, 2015.
[19]. A. C. F. M. Costa, A. P. Diniz, V. J. Silva, R. H. G. A, Kiminami, D. R. Carnejo, A. M. Gama, M. C. Rezende, L. Gama, "Influence of calcination temperature on the morphology and magnetic properties of Ni-Zn ferrite applied as an electromagnetic energy absorber", *Journal of Alloys and Compounds*, 483, 563-565, 2009.