Effects of washing method of nickel slag to the structural properties of composite nickel slag/laterite soil for high electromagnetic wave absorption performance

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Abstract. Laterite soil (LS) doped with nickel slag (NS) for different solvent was successfully use to enhance the microwave absorption properties. First, NS/LS-01 is laterite soil doped with nickel slag for washed by using hydrogen chloride and second, NS/LS-02 for nickel slag washed by using sodium chloride. All samples are prepared by milling method at low frequency (10 Hz). X-ray diffraction (XRD) result revealed that the as polycrystalline of a cubic phase and diffraction spectra were dominated by magnetite (Fe₃O₄). X-ray peak broadening was analyzed to evaluate the structural properties. The quantitative analysis of structural properties in this studies are Scherrer, Williamson-Hall and Size strain plot method. Crystallite size (D), micro strain (ε), stress (σ) and energy density (u) were extracted from the peak line broadening. NS/LS-02 shows the smallest volume lattice, the energy density and the best reflection loss (RL) from the vector network analyzer (VNA). It is reveals the unit cell with high energy density strong relationship with microwave properties. In this study easy method to find the best correlation between structural and microwave properties.

1. Introduction
The electromagnetic interference wave is a new pollution for this era, which impacts to the human health [1]. The scientist in the world looking for new materials to solve the problem caused by electromagnetic interface, In this paper focus for utilizing the magnetite particle from laterite soil and nickel slag as microwave absorbent, composite with easy to produce the be a microwave absorbing materials (MAM). However to get the best performance from absorbent [1-3], the relationship between absorbent thickness and reflection loss in (dB) is fundamental knowledge for this purposes. Laterite soil (LS) and nickel slag (NS) are suitable material for MAM due to the magnetite content [4]. Another reason, LS and NS are low cost, have excellent magnetite properties. The research about magnetite such as inelastic mean free path [5-7] and magnetite ability as a shielding of x-ray [8]. For laterite soil is an prospective soil, so utilizing the laterite soil as microwave absorbent will be additional function, and from ecological view, the abundance of nickel slag that produced by nickel industrial is a crucial waste which a problem for producer country.

For improving the quality of microwave absorbent, the magnetite (Fe₃O₄) was reported by ref [9]. The dominating of Fe₃O₄ compound on the LS/NS bulk were prepared by milling method, The NS this study washed by two methods where the NS-01 by sodium chloride and NS-02 by hydrogen chloride. The LS doped by NS-01 and NS-02 affected to the structural and microwave properties. The lattice
parameter determined by using Bragg equation, the relation between the cell length ($a$) as the structural properties and the absorption has not been reported. X-ray diffraction (XRD) spectra at $2\theta = 15^\circ - 65^\circ$ and reflection loss by using vector network analyzer (VNA) in the range 2-8 GHz.

2. Experimental
Laterite soil taken from around campus of Hasanuddin university. The nickel slag is the primer solid waste from nickel industries in Sulawesi, Indonesia. The first step grinding the NS by using the Jaw Crusher W 200 until became powder with size 80 mesh (177 micron). SN-01 washed by using hydrogen chloride, and keep it for 24 hours at room temperature, wash by using aqua-bides until pH $\approx$ 7 and warmed it at 60$^\circ$C. For SN-2 same step with SN-01 but used by sodium chloride. The powder of NS and LS were mixing by using RETCSH MM 400 at the frequency 10 Hz for 30 minutes to form binary powder LS/SN. 5 grams (LS = 4.8 gram and NS = 0.2 gram) of LS/NS powders added slowly the PVA with comparison 5:3. All samples mixed again with magnetic stirrer 400 rpm at 40$^\circ$C. The final step, all samples put in sample holder with a diameter of 1 cm and drying in 24 hours, then pressed at 10 bars.

The XRD instrument condition and preparation as following our previous work ref. [10] and for VNA method, detail explanation is in Abdullah’s work [11].

3. Result and discussion
3.1 X-Ray diffraction
X-ray diffraction spectra are shown in Figure 1a for LS, LS/NS-01 and LS/NS-02. The diffraction peak for all domination is Fe$_3$O$_4$ were it use for analyzing the crystallite size (D), strain ($\varepsilon$), stress ($\sigma$) and energy density ($u$).

![Figure 1. X-ray diffraction spectra showing the Miller indices (a) and the strain using Scherrer (b). The samples: LS (red-line), LS/NS-01 (black-line), and LS/NS-02 (blue-line)](image)

Figure 1a confirm that the solvent affected to the intensity spectra of LS, the lowest for LS doped with SN-01 and the LS doped SN-02 is highest. Than Figure 1a also confirm that, all samples shows the dominant by magnetite phase with cubic structure. That’s all spectra will use to evaluate the Crystallite size (D), micro strain ($\varepsilon$), stress ($\sigma$) and energy density ($u$) were extracted from peak line broadening by using Scherrer, Williamson Hall and Size strain plot method (SSP).

For Figure 1b the Scherrer equation used to find the relation $\varepsilon$ and $2\theta$ that mean that the d-spacing (d) is directly proportional. According to our previous work [12-13], the Scherrer equation, Williamson Hall method (uniform density method) and SSP respectively can be written as:

$$D = \frac{k\lambda}{\beta\cos\theta}, \text{where } \beta = \left(\beta^2 + \beta^2_{\text{ins}}\right)^{1/2}$$ (1)
Equation 1 is Scherrer equation, where $\beta$ is the full width half maximum (FWHM) where we can get from $\beta_s$ as measured and $\beta_{\text{ins}}$ as FWHM from standard sample and corrected by instrument. The line broadening is affected by $D$ and $\varepsilon$ of the diffraction spectra. The line broadening is a product by size and strain, as follows:

$$
\beta = \frac{k\lambda}{D\cos\theta} + 4\varepsilon \tan \theta, \text{ multiply by } \cos \theta
$$

$$
\beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta
$$

Equation 2 is Williamson hall method on the uniform density model. By this model, assume that the strain on the lattices structure is uniform, so it can be translated the W-H UDM will produces the one value of crystallite size and strain. Another way to find the structural properties usually use the SSP method [13] as effort to get the good correlation for all calculations, the equation as follows [14]:

$$
(d\beta_{hkl}\cos \theta)^2 = \frac{k}{D} (d^2 \beta_{hkl}\cos \theta) + \left(\frac{\varepsilon}{2}\right)^2
$$

From SSP method (eq. 3), $\varepsilon$ is determined by using Gaussian function and the D as crystallite size is determined by Lorentz function. All result from the equation 1-3 presented in the Table 1 and Figure 2.

**Figure 2.** For the UDM model (the size extracted from y intercept and strain extracted from the slope) and the SSP method (the crystallite size is determining from slope and micro strain from the y-intercept by using linear fitting methods)

Table 1 is presented the average crystallite size for all calculation, which shows the doping NS does not influenced to the crystallite size, whereas the NS-01 and NS-02 clearly make the energy density going to be lowest and highest respectively. Another calculation is the lattice condition by the Bragg’s equation for cubic crystal, presented in Table 2.

From Table 2 the unit cell from LS/NS-02 has smallest and LS have a highest unit cell volume in Å$^3$. Knowledge of lattice parameters condition is essential for search the suitably of composite in absorbing EM wave [15]. In this study, the relation between cell length and reflection loss for all samples is discussed below.
Table 1. Crystallite size (D), strain (ε), energy density (u), by using Scherrer, W-H and SSP from quantitative analysis of XRD spectra in Figure 1a. for LS, LS/NS-01, and LS/NS-02.

| Sample       | ( h k l ) | Scherrer        | Williamson Hall | Size Strain Plot |
|--------------|----------|-----------------|-----------------|------------------|
|              |          | D (nm) | E   | D (nm) | ε    | D (nm) | ε    | σ (MPa) | U    |
| Laterite Soil (LS) | 111     | 13.716   | 0.017 | 19.1 | 0.00313 | 9.97 | 0.011 | 203 | 118.8 |
|              | 202     | 14.833   | 0.0088 |      |          |      |        |     |        |
|              | 131     | 12.366   | 0.0095 |      |          |      |        |     |        |
|              | 40      | 15.789   | 0.0064 |      |          |      |        |     |        |
|              | 151     | 10.665   | 0.0075 |      |          |      |        |     |        |
|              | 404     | 9.8366   | 0.0072 |      |          |      |        |     |        |
| LS/NS-01     | 111     | 12.1581  | 0.018 | 11.13 | 0.00173 | 11.662 | 0.0093 | 163.37 | 76.6 |
|              | 202     | 14.9391  | 0.0092 |      |          |      |        |     |        |
|              | 131     | 12.2108  | 0.0099 |      |          |      |        |     |        |
|              | 40      | 18.2019  | 0.0055 |      |          |      |        |     |        |
|              | 151     | 14.8547  | 0.0053 |      |          |      |        |     |        |
|              | 404     | 15.4322  | 0.0046 |      |          |      |        |     |        |
| LS/NS-02     | 111     | 13.6155  | 0.0154 | 11.61 | 0.004061 | 7.603 | 0.01299 | 227.4 | 147.8 |
|              | 202     | 18.7902  | 0.0072 |      |          |      |        |     |        |
|              | 131     | 6.5957   | 0.0186 |      |          |      |        |     |        |
|              | 40      | 13.6917  | 0.0075 |      |          |      |        |     |        |
|              | 151     | 12.4144  | 0.0064 |      |          |      |        |     |        |
|              | 404     | 11.535   | 0.0063 |      |          |      |        |     |        |

Table 2. Lattice parameter (a) for a cubic crystal of LS, LS/NS-01, and LS/NS-02

| Sample       | a (cell length) Å | max Volume (Å³) | d-spacing (Å) |
|--------------|-------------------|-----------------|---------------|
| LS           | 8,328319          | error : 0,021884| 582,225337    | 2,48 |
| SN/LS-01     | 8,32758           | error : 0,009433| 579,4706395   | 2,47 |
| SN/LS-02     | 8,30561           | error : 0,007135| 574,4250559   | 2,45 |

Figure 3. Reflection Loss (dB) with several screen (plot, contour and surf)
3.2 Vector network analyzer (VNA)

Figure 3. Show the effect of solvent to the ability in absorbing EM wave. In the Figure 3 the LS/NS-02 composition shows the lowest reflection loss (RL) indicated successfully of solvent sodium chloride in increasing magnetite properties [16]. The treatment of solvent also presents the tiny shifted to the higher working frequency, and the absorption width when it calculated from RL = 10 dB and RL = 20 dB. The effective absorption bandwidth for LS is 2.75 GHz, for LS/NS-01 is 2.35 GHz and LS/NS-02 is 2.75 GHz for measurement at RL: 10dB and LS is 0.74 GHz, for LS/NS-01 is 0.76 GHz and LS/NS-02 is 1.02 GHz for measurement at RL: 20dB. The result of electromagnetic wave absorption performance is corresponding to crystalline phase (Figure 1a) and the effect of solvent, the lowest crystalline phase (LS) have highest RL and the highest crystalline for LS/NS-02 have the lowest RL value. The penetration of electromagnetic waves is also influenced by the volume of the unit cell, this can be observed from table 2 where the LS with the largest volume has value of RL is -27.8 dB and LS / NS-02 with the smallest cell volume size has value of RL is -38.67 dB. In this study show new composite by simple preparation method high potential for absorption EM wave.

4. Conclusion

In this work, we successfully produce absorbent from two type of solvent on the LS/NS composite to enhance their ability to absorb the electromagnetic wave. Material was analyzed by using x-ray diffraction to evaluate the relation between structural properties and microwave absorption as a guide to improve electromagnetic wave absorption performance by using sodium chloride.

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