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RESEARCH ARTICLE

Modification of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$: Influence of Ni-substitution on the magnetic properties

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Abstract

In this study, the synthesis of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ with variations in composition (x = 0.01, 0.05, 0.1, and 0.15) using a mechanical milling technique has been performed. High purity powder of α-Fe_2O_3, TiO_2, $MnCO_3$, and NiO were prepared as raw materials. The mixture was milled for 5 hours using high energy milling equipment, and sintered at 1000 °C for 5 hours. The refinement result of X-ray diffraction profile shows that the all of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ samples have a single phase with particle size of less than 1 μm. The VSM result shows all the samples were ferromagnetic behavior. We concluded that the substitution Ni into Mn on the pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ can change the magnetic properties of the material from paramagnetic to ferromagnetic through a mechanism of double exchange interaction.
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Keywords: Pseudobrookite, $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$, milling, modification, magnetic properties

INTRODUCTION

Pseudobrookite is an iron titanium oxide mineral with the formula of Fe_2TiO_5 (Ferric pseudobrookite). This material is usually brown or black in colors with an orthorhombic crystal structure. Ferric pseudobrookite of Fe_2TiO_5 exhibits an interesting anisotropic-uniaxial spin-glass state at low temperature and like other Fe-Ti-oxides, it has potentials to be used in microelectronics, gas sensing, non-linear optics, and magnetic applications. While it is not a commonly occurring mineral, the pseudobrookite sparks interest in both commercial and scientific applications. The pseudobrookite is produced in substantial quantities during the processing of ilmenite ores as a by-product of iron and titanium extraction (Mahmoud et al., 2018; Hoed et al., 2011; Aljuraide et al., 2011; Seitz et al., 2016).

Pseudobrookite can be obtained from the ilmenite phase transformation at temperatures above 900 °C. In addition, this ilmenite mineral is one of the biggest phases in iron sand (Xiao, et al., 2013; Sarwanto et al., 2015; Adi et al., 2015; Liu et al., 2014; Ramezani et al., 2015). In the previous research, a smart magnetic material for electromagnetic wave absorbing material has been developed (Hajalilou et al., 2016; Chen et al., 2015; Idris et al., 2016; Ponmani et al., 2018). The material requires the presence of several intrinsic characteristics, i.e. magnetic loss and dielectric loss on the material (Adi et al., 2019; Petit et al., 2016). The presence of titanium in the Fe_2TiO_5 pseudobrookite system allows this material to have good permittivity. Therefore, various approaches have been carried out to improve the magnetic properties of this material (Gao et al., 2015; Narang et al., 2016).

In the previous study, manganese (Mn) has been successfully substituted into iron (Fe) on this pseudobrookite materials by using mechanical milling technique. The refinement pattern of X-ray diffraction samples of pseudobrookite $Fe_{2-x}Mn_xTiO_5$ show that the sample has a single phase in the composition x = 0.1 – 0.3. According to the SEM image, it appears that it has a good particle homogeneity, uniform and a polygonal particle shape. The substitution Mn into Fe on the pseudobrookite $Fe_{2-x}Mn_xTiO_5$ only capable of x ≤ 0.3 at% without changing its crystal structure, the rest was found another phase. However, while the results of its magnetic properties on the composition of x < 0.3 still behave paramagnetic, meaning the value of permeability is still low (Sarwanto et al., 2019). For that, further modification is necessary to improve the permeability by making the material has ferromagnetic behavior.

This study has performed modification through material engineering on the pseudobrookite material of $Fe_{1.7}Mn_{0.3}TiO_5$ with the substitution of nickel (Ni) atoms in Mn atom. Ni is expected to able to replace a part of the position of the Mn atoms so that the exchange interaction between the magnetic spin Fe^{3+} and Mn^{3+} with Ni^{2+} ions and can affect the magnetic properties of this material through double exchange mechanism. The purpose of this research is to synthesize and determine the effect of Ni substitution on the magnetic properties of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ material with variations in composition (x = 0.01, 0.05, 0.1, and 0.15).

EXPERIMENTAL

Pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15) was synthesized trough solid state reaction by using mechanical milling method. High purity powders of α-Fe_2O_3, TiO_2 (anatase), $MnCO_3$, and NiO were prepared as raw materials from Aldrich and Merck products. All of the raw materials were weighed based on the calculation result of stoichiometric composition and then mixed. The mixture was milled for 5 hours using high energy milling equipment of PW1000 mixer/mill. After that, the mixture was dried and sintered at 1000 °C for 5 hours in a furnace of thermolyne product. Phase analysis of the sample was measured by using X-ray diffractometer (XRD) from Pan Analytical with X-ray tube with a wavelength of λ = 1.5406 Å (Cu-Kα), and the crystal structure was analyzed by using GSAS software. The particle morphology and element content were observed by using scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) from JEOL brand. Meanwhile, the magnetic properties were measured by using vibrating sample magnetometer (VSM) from Oxford product.

RESULTS AND DISCUSSION

In the previous study, a single sample of $Fe_{1.7}Mn_{0.3}TiO_5$ pseudobrookite samples was obtained based on the analysis of X-ray diffraction patterns as shown in Figure 1 (Sarwanto et al., 2017). This means that substitution of Mn atoms into some of the Fe atoms in the pseudobrookite system has been successfully performed. This becomes a reference to qualitatively identify the samples that have been synthesized in this study.

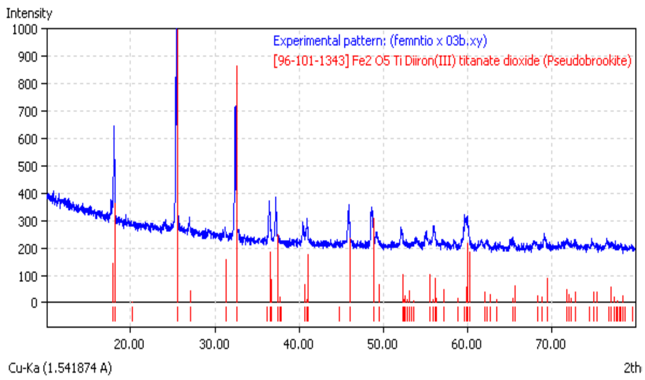


Figure 1 Phase identification of XRD pattern on the sample $Fe_{1.7}Mn_{0.3}TiO_5$.

Figure 2 shows the results of measurements of X-ray diffraction pattern of the sample pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ with variations in composition (x = 0.01, 0.05, 0.1, and 0.15).

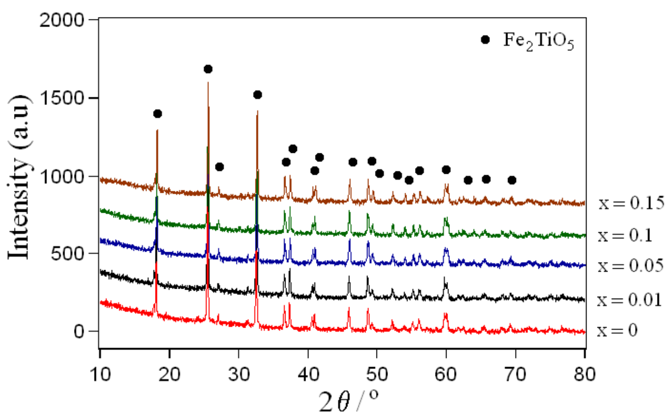


Figure 2 XRD pattern of the sample Fe1.7Mn0.3-xNixTiO5 (x = 0.01, 0.05, 0.1, and 0.15).

Referring to the phase identification, it qualitatively appears that the XRD profile for all of samples were similar profiles with XRD profile of sample pseudobrookite $Fe_{1.7}Mn_{0.3}TiO_5$. It indicates that the all of sample have been successfully formed a single phase of Fe_2TiO_5. The results of phase identification are very interesting to understand due to that the atoms of manganese have succeeded in substituting partially of the atoms Fe in the structure $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15). Next, to know the effect of Ni substitution on the changes of the crystal structure parameters and

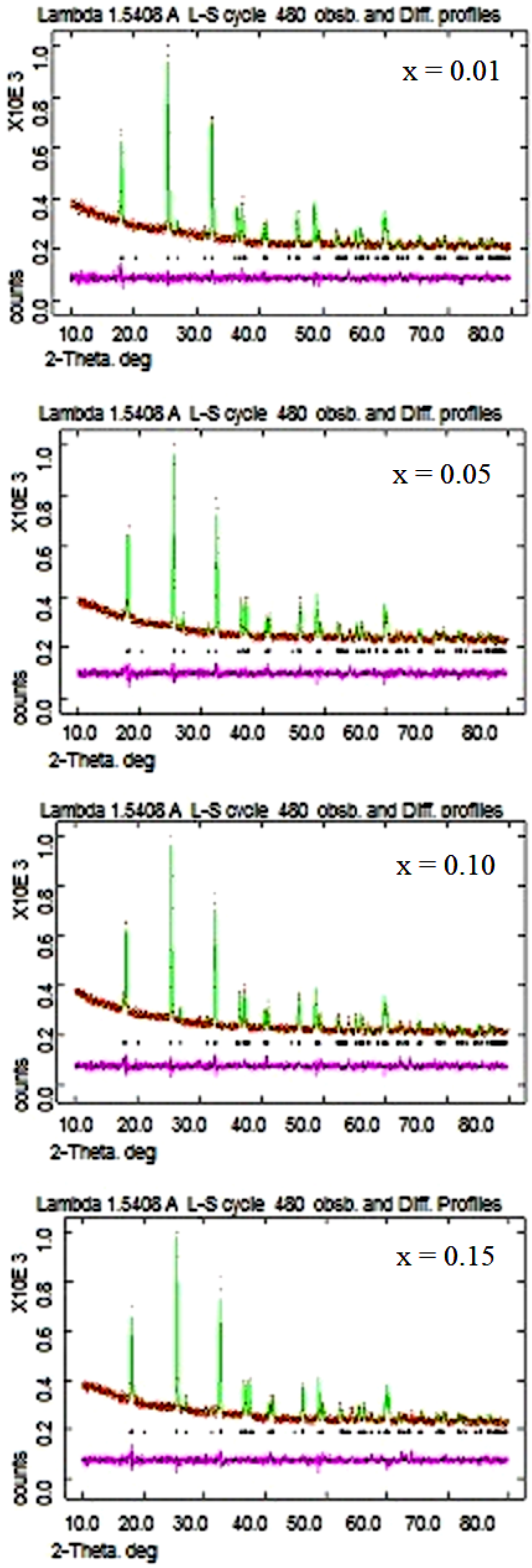


Figure 3 The refinement results of XRD pattern on the samples of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$.

the amount of mass fraction formed, further analysis was required by using GSAS program as shown Figure 3.

Figure 3 shows the results of refinement X-ray diffraction pattern of the sample pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ with variations in composition (x = 0.01, 0.05, 0.1, and 0.15), in which that have been formed Bragg diffraction peaks with a single phase following the Fe_2TiO_5 structure (Xiao et al., 2013; Sarwanto et al., 2019). Both the qualitative and quantitative analyses refer to the Crystallography Open

Database with the card number (COD: 1011342) for phases of Fe_2TiO_5. Detailed summary of the refinement results of X-ray diffraction pattern of the sample pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15) for all of samples are shown in Table 1.

Table 1 The value of structure parameters, criteria of fit (R_{wp}), goodness of fit (χ2), and the mass fraction of phase formed in the sample pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15).

x	Ni content			
	0.01	0.05	0.1	0.15
Phase	Fe_2TiO_5	Fe_2TiO_5	Fe_2TiO_5	Fe_2TiO_5
Lattice parameter (Å)	a = 3.7316(2) b = 9.7780(6) c = 9.9588(5)	a = 3.7315(2) b = 9.7753(6) c = 9.9575(5)	a = 3.7311(1) b = 9.7708(6) c = 9.9552(5)	a = 3.7309(2) b = 9.7674(6) c = 9.9536(5)
V (Å^3)	363.38(4)	363.24(4)	362.93(4)	362.82(4)
ρ (g/cm^3)	4.353	4.355	4.359	4.360
Fraction (wt%)	100.00	100.00	100.00	100.00
Rw (%)	3.35	3.35	3.40	3.42
χ^2	1.28	1.30	1.31	1.32

The refinement results, the quality of fitting χ^2 (goodness of fit) factors should be in the range of 1.275 – 1.296. The number of fitting results between those range means that the actual data and the diffraction data base shows a good and reliable match. As shown in Table 1, the results of this refinement resulting inan excellent fitting quality with a very small R factor. The R factor is the criteria of fit and the S factor is the goodness of fit which is of very small value. and according to Toby the value of S or χ^2 (chi-squared) is allowed to maximum 1.3 (Toby, 2001).

As tabulated in Table 2, it is apparent that the samples have decreased volume of the unit cell meanwhile the atomic density increase along with increasing the composition x. This is due to the ionic radius Ni^{2+} (r = 1.62 Å) is shorter than the ionic radius of Mn^{2+} (r = 1.79 Å) and Fe^{2+} (r = 1.72 Å), thus resulting in lattice parameter also decrease for the third of axis. Because the number of atoms is considered constant while the unit volume of the cell decreases causing its atomic density to increase. In our previous study of the substitution of Mn into Fe atoms has the same phenomenon that because the radius of Mn ion is greater than Fe ion, the volume of cell units increases and the atomic density decreases (Sarwanto et al., 2017). These refinement results are also supported by observations of the surface morphology of particles for single phase using scanning electron microscope (SEM) and the present of this Mn and Ni can be proved base on the result of energy dispersive spectroscopy (EDS) data as shown in Figure 4.

In Figure 4, the particle morphology of the all samples have a good particle homogeneity and uniform with an aggregated particle shape, and the particle size varies less than 1 µm. The results of elemental analysis using EDS in detail for all samples of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15) for all of samples are shown in Table 2.

The results of semi-quantitative analysis of the element content indicate that the Ni atom content increases with the addition of the composition x. This proves that the result of phase analysis using XRD data has successfully formed single phase with data of composition support using EDS test result.

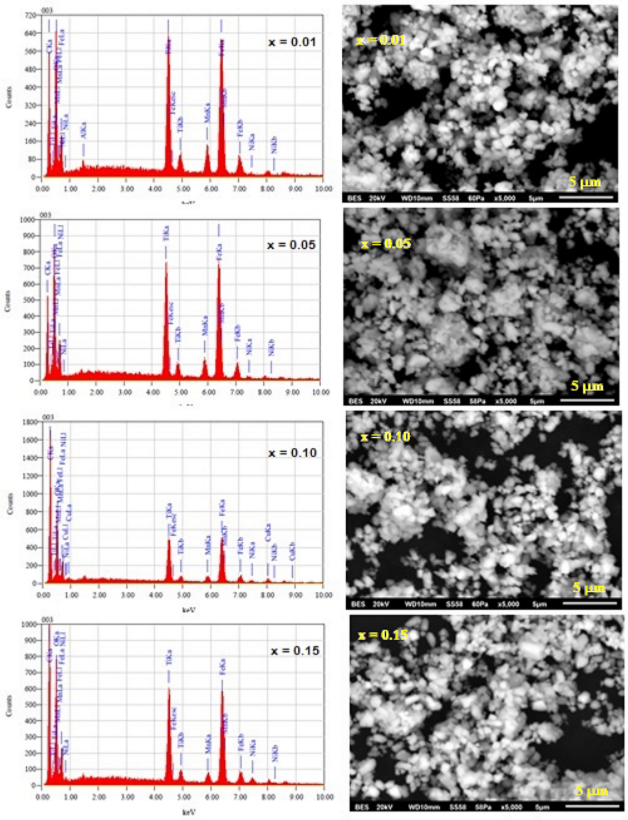
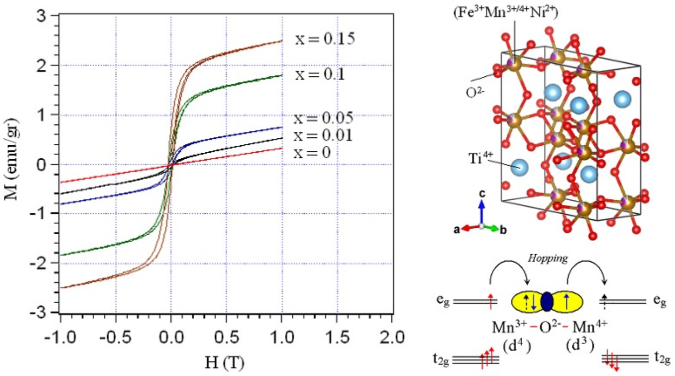


Figure 4. SEM-EDS results of the sample of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$.

Table 2 Element distribution on the Fe1.7Mn0.3-xNixTiO5 was measured by EDS.

Element	Energy (keV)	Norm. Mass fraction (%)			
		x = 0.01	x = 0.05	x = 0.10	x = 0.15
O	0.525	41.47	43.19	56.31	50.06
Ti	4.508	17.52	16.51	12.68	14.89
Mn	5.894	5.66	4.38	2.83	2.12
Fe	6.398	35.1	34.97	26.56	30.59
Ni	7.471	0.25	0.95	1.62	2.34

The result of characterization of magnetic properties in pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15) samples for all of samples is shown in Figure 5. Figure 5(a) is the hysteresis curve of the pseudobrookite sample showing intrinsic characteristics become parameters of magnetic properties of materials, namely coercivity field (Hc), remanent magnetization (Mr), and saturation magnetization (Ms). Based on this hysteresis curve, it can be identified that the sample behave paramagnetic or ferromagnetic. An important requirement is that a material is ferromagnetic if they have these three magnetic parameters. It is not possessed by a paramagnetic material. Referring to Figure 5, the magnetic parameters of both Hc, Mr, and Ms on the pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ (x = 0.01, 0.05, 0.1, and 0.15) samples are shown in Table 3. In Figure 5(a), it appears that there has been a transformation of magnetic properties from paramagnetic to ferromagnetic after this pseudobrookite sample is substituted with Ni atoms. The ferromagnetic properties are stronger as the composition of x increases. The transformation of the magnetic phase from paramagnetic to ferromagnetic occurs due to the presence of substitution of Ni atoms in Mn atoms located at one Fe atomic site at the atomic position coordinates (0, 0.135, 0.56).



(a) (b)

Figure 5 The hysteresis curve of the pseudobrookite $Fe_{1.7}Mn_{0.3-x}NixTiO_5$ by using VSM

Table 3 Magnetic parameters of the $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ was measured by using VSM.

x	Properties	Magnetic parameters		
		Hc (Oe)	Mr (emu/gr)	Ms (emu/gr)
0.01	Ferromagnetic	160	0.03	0.50
0.05	Ferromagnetic	165	0.10	0.75
0.1	Ferromagnetic	170	0.26	1.80
0.15	Ferromagnetic	210	0.52	2.50

The presence of Ni^{2+} ions which replaced some of the Mn^{3+} ion positions affected the change of Mn^{3+} ion valence become to mixed valence Mn^{3+}/Mn^{4+} in order for the electron configuration on the Fe atomic site to remain stable. While the presence of mixed valence Mn^{3+}/Mn^{4+} results in a magnetic exchange spin interaction between Mn^{3+} and Mn^{4+} adjacent atoms through O^{2-} intermediaries through a double exchange interaction mechanism as shown in Figure 5(b) (Sardjono et al., 2014). This exchange interaction increases with increasing mixed valence between Mn^{3+}/Mn^{4+} in the materials. This means that the ferromagnetic properties of the material get stronger as the amount of mixed valence more and more as a result of the amount of Ni substitution in Mn increases. In other words, the increase in saturation magnetization is not caused by an increase in the number of dipole moments with the presence of nickel ions, but because this double exchange interaction increases after the presence of Ni ions. As a result, the number of spin orientations in the magnetic domain increases, ultimately the remanence magnetization and coercivity field also increase. Thus, the interesting thing of this research is that pseudobrookite-based materials have been successfully engineered and produced a single phase with the same structure, but their magnetic properties are different.

CONCLUSION

Synthesis of pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ with variations in composition (x = 0.01, 0.05, 0.1, and 0.15) has been successfully carried out and the influence of substitution of Ni on the magnetic properties of the material has been studied in details. The refinement pattern of X-ray diffraction samples pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ shows that the all of samples have a single phase with a particle shape and the particle size varies. The substitution Ni into Mn on the pseudobrookite $Fe_{1.7}Mn_{0.3-x}Ni_xTiO_5$ can change the magnetic properties of paramagnetic to ferromagnetic through the mechanism of double exchange interaction.

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