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Structure analysis of electromagnetic waves absorbing material a lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$

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Structure analysis of electromagnetic waves absorbing material a lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$

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Abstract. Solid compound of lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$ has been synthesized via conventional solid state reaction route using lanthanum oxide (La_2O_3), barium carbonate (BaCO_3), zinc oxide (ZnO), ferric oxide (Fe_2O_3) and manganese carbonate (MnCO_3) powders as it raw materials. High energy ball milling was used to mix the material for 5 hours. It is then sintered at 1000°C for 5 hours. X-ray powder diffraction method (XRD) and scanning electron microscopy (SEM) was used to analyze the change of structure of the solid compound. The refinement pattern result of the XRD shown that a single phase was occurred in the form of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$. It has trigonal lattice crystal structure of (r-3c) point group with lattice parameter of $a = b = 5.515 \text{ \AA}$ and $c = 13.551 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, a volume unit cell of $V = 356.904 \text{ \AA}^3$ and a density of $\rho = 6.745 \text{ g.cm}^{-3}$. The SEM result shown that the surface morphology of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$ has a homogeneous sphere structure. The XRD and SEM structure analysis result of the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$ shown that the compound is feasible for further studied.

1. Introduction

In recent years the use of electromagnetic waves based technology for applications are rapidly grown. One of it was telecommunications technology. The growth of the telecommunications technology provider is in line with the growth of the electromagnetic waves radiation on earth's atmosphere. This phenomenon has bad influence on other electronic devices that used the same technology, resulting from noise to error [1]. It is believed that the electromagnetic waves radiation originated from cellular phone signal could trigger the emergence of cancer cell [2]. It is also believed that a magnetic material which resonate at certain frequency and absorb hazardous electromagnetic waves radiation could reduce the problem, an electromagnetic waves absorbing material [3].



An electromagnetic waves absorbing material must have high permeability (magnetic loss properties) and high permittivity (dielectric loss properties) [4]. A modification of ferrite based magnetic material resulting in high permeability [5] and manganese based magnetic material with perovskite crystal structure resulting in high permittivity are the thriving studies of electromagnetic waves absorbing material nowadays. This type of material combined with material structure engineering could create prime material for electromagnetic waves absorbing material applications [6]. The modification of the lanthanum manganite system by substituting certain element inside lanthanum manganite system ions which in turn influence the magnetic properties and the material structure has been studied and done [7-9].

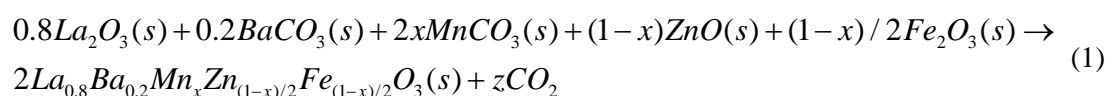
The magnetic structure of LaMnO_3 is anti-ferromagnetic. Magnetic interactions in this system belong to the indirect exchange interaction, called superexchange mechanism. Superexchange mechanism is the magnetic interaction between the adjacent Mn^{3+} ions mediated by nonmagnetic ions O^{2-} with electron spin pairing. The hysteresis curve of LaMnO_3 measured at room temperature has a linear magnetic pattern as a function of the applied magnetic field. Meanwhile the presence of Ba substitution into La on this system causes a magnetic phase transformation. In contrary, the magnetic structure of $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ is ferromagnetic. This magnetic phase transformation occurs due to the presence in the mixed valence Mn through double-exchange mechanism. The mechanism of double exchange is the magnetic interaction in which the displacement of the electron spin is parallel to the nearest neighbor by doing twice hopping simultaneously from Mn^{3+} ions to Mn^{4+} ions through O^{2-} ions. The hysteresis curve of $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ measured at room temperature has a nonlinear magnetic pattern as a function the applied magnetic field [8].

A modification of the lanthanum manganite system of $(\text{LaSr})\text{MnO}_3$ with ferrite ion (Fe^{+3}) as an injector which result in the empirical formula of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$ ($0 < y < 0.2$) has been done. The ferrite (Fe) addition of $y = 0.14$ increase the material reflection loss value up to -34 dB with an absorption percentage value of 98% and it is believed that the addition of ferrite ion gives huge contribution to the magnetic properties of the material [9]. A research of lanthanum manganite system of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ has been done and it resulting in two peak wave absorption which occurred at frequency of 11.1 GHz and 14.2 GHz with reflection loss value of -4.8 dB and -6.8 dB and an absorption percentage value of 55% [10].

In this research, we will present structural engineering materials called perovskite $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$, where the element iron is substituted with manganese (Mn) to increase its permeability and zinc (Zn) to increase the permittivity in the material. The focus of discussion is to determine the material structure due to addition of iron and zinc.

2. Materials and methods

A lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$ with ferrite ion (Fe^{+3}) and zinc ion (Zn^{+2}) as an injector will be synthesized via conventional solid state reaction route using lanthanum oxide (La_2O_3), barium carbonate (BaCO_3), zinc oxide (ZnO), ferric oxide (Fe_2O_3) and manganese carbonate (MnCO_3) powders as it raw materials. The mixing of these raw materials will be done using stoichiometry principle as shown in equation;



The concentration of ferrite ion (Fe^{+3}) and zinc ion (Zn^{+2}) injection into manganese ion (Mn^{+2}) will be varied which is $x = 0$, $x = 0.2$, $x = 0.4$ and $x = 0.6$. High energy ball milling with normal speed setting at 90 minute, off time at 30 minute and on off cycle for one time will be used to mix the raw materials

for 5 hours at room temperature. It is then sintered at 1000°C for 5 hours and then cooled at room temperature.

The x-ray powder diffraction (XRD) instrument of PANalytical then used to identify the phase of each sample compound. The Rietveld method with refinement parameter [11] will be used to analyze the phase of each sample compound. The scanning electron microscopy (SEM) instrument of scanning electron microscope – energy dispersive spectroscopy (SEM-EDS) JEOL JSM-6510LA will be used to analyze the surface morphology and compound compositions analysis of each sample compound.

3. Result and discussion

3.1 Phase analysis

Phase analysis of the compound with varied concentration of injector is determined by comparing and matching the x-ray diffraction pattern data acquired of each compound with the data from crystallography open database (COD). The x-ray diffraction pattern of lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ for each compound is shown in Figure 1.

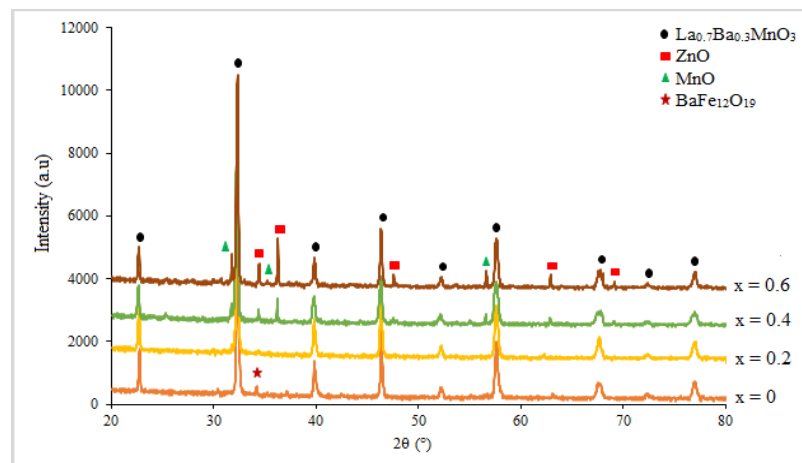


Figure 1. X-ray diffraction pattern of lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$.

It is shown in Figure 1 that there are several phase occurred in each of the sample compound of the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$. The x-ray diffraction pattern for sample compound with concentration $x = 0$ and it peaks identification shown that the pattern was not of single phase. A phase of $BaFe_{12}O_{19}$ occurred and matches the data from COD No. 96-100-8327 alongside a phase of $La_{0.7}Ba_{0.3}MnO_3$ which matches the data from COD No. 96-400-2491. The x-ray diffraction pattern for sample compound with concentration $x = 0.2$ and it peaks identification shown that the pattern was of single phase. The only single phase was of $La_{0.7}Ba_{0.3}MnO_3$ which matches the data from COD No. 96-400-2491. The x-ray diffraction pattern for sample compound with concentration $x = 0.4$ and $x = 0.6$ and it peaks identification shown that the pattern was not of single phase. A phase of MnO which matches the data from COD No. 96-411-7967 and a phase of ZnO which matches the data from COD No. 96-230-0116 occurred alongside a phase of $La_{0.7}Ba_{0.3}MnO_3$ which matches the data from COD No. 96-400-2491. In conclusion, the single phase occurred in the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.4}Zn_{0.2}Fe_{0.4})O_3$.

A refinement analysis process of the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ will be done to analyze the effect of ferrite ion (Fe^{+3}) and zinc ion (Zn^{+2}) injection to the compound regarding its main structure element using Match!3 program and general structure analysis system (GSAS) software.

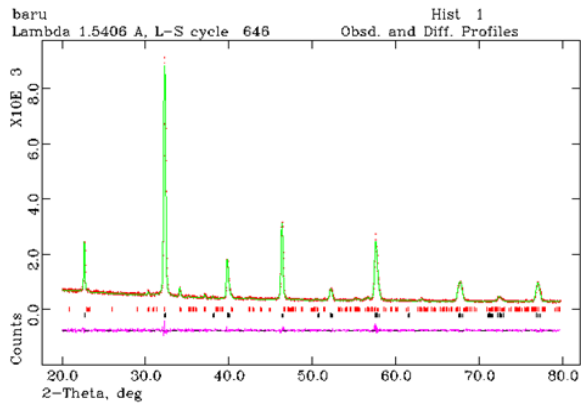


Figure 2. X-ray diffraction refinements pattern of lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.5}Fe_{0.5})O_3$ ($x = 0$)

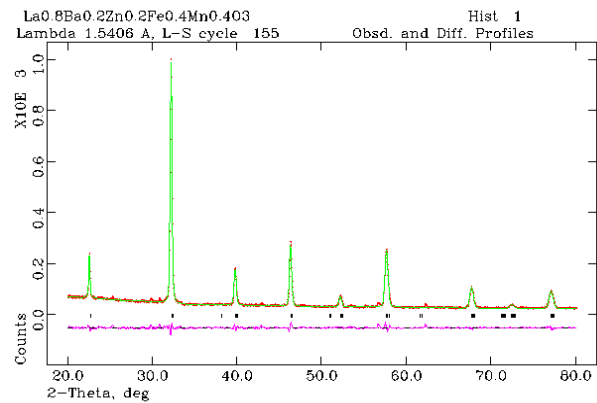


Figure 3. X-ray diffraction refinements pattern of lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.4}Zn_{0.2}Fe_{0.4})O_3$ ($x = 0.2$)

It is shown in Figure 2 that there are two phases occurred in the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.5}Fe_{0.5})O_3$ ($x = 0$) which is a phase of $La_{0.7}Ba_{0.3}MnO_3$ and a phase of $BaFe_{12}O_{19}$. A phase of $BaFe_{12}O_{19}$ occurred because at injector concentration of $x = 0$, the ferrite ion (Fe^{+3}) already injected into the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$. It is shown in Figure 3 that there is a single phase occurred in the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.4}Zn_{0.2}Fe_{0.4})O_3$ ($x = 0.2$) which is a phase of $La_{0.7}Ba_{0.3}MnO_3$. A phase of $La_{0.7}Ba_{0.3}MnO_3$ is belongs to the trigonal lattice crystal structure of (r-3c) point group. One cell of trigonal lattice contain 18 oxide ion (O^{-2}), 6 lanthanum ion (La^{+3}), 6 barium ion (Ba^{+2}) and 6 manganese ion (Mn^{+2}). The lanthanum (La), barium (Ba), manganese (Mn) and oxygen (O) atom occupied the Wyckoff position of 6a, 6a, 6b and 18e respectively.

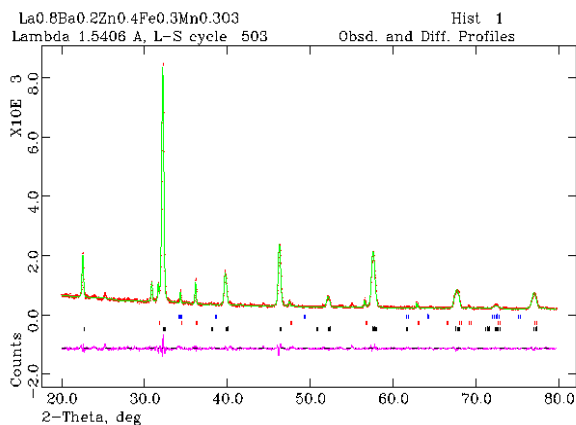


Figure 4. X-ray diffraction refinements pattern of lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.3}Zn_{0.4}Fe_{0.3})O_3$ ($x = 0.4$)

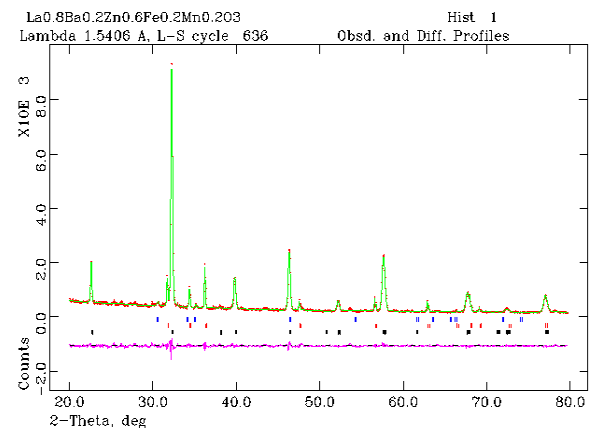


Figure 5. X-ray diffraction refinements pattern of lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.2}Zn_{0.6}Fe_{0.2})O_3$ ($x = 0.6$)

It is shown in Figure 4 and Figure 5 that there are three phases occurred in the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.3}Zn_{0.4}Fe_{0.3})O_3$ ($x = 0.4$) and $(La_{0.8}Ba_{0.2})(Mn_{0.2}Zn_{0.6}Fe_{0.2})O_3$ ($x = 0.6$) which is a phase of $La_{0.7}Ba_{0.3}MnO_3$, a phase of MnO and a phase of ZnO. The injection of ferrite ion (Fe^{+3}) and zinc ion (Zn^{+2}) with concentration of $x = 0.4$ and $x = 0.6$ into the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ generated a new phase of MnO and a phase of ZnO. The phase identification method for the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ with

injector concentration of $x = 0$, $x = 0.2$, $x = 0.4$ and $x = 0.6$ in this research is in accordance with the referenced literature [12,13].

The lattice structure parameter value, criteria-of-fit (Rwp) value, goodness-of-fit (χ^2) value and the mass fraction of phase formed of the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ for each sample compound is shown in Table 1.

Table 1. The lattice structure parameter value, criteria-of-fit (Rwp) value, goodness-of-fit (χ^2) value and the mass fraction of phase formed of the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$

Sample (x)	Phase	Lattice parameter (Å)			V (Å ³)	ρ (g/cm ³)	Fraction Wt%	R _{wp} (%)	χ^2
		a	b	C					
0	La _{0.7} Ba _{0.3} MnO ₃	5,543	5,543	13,508	359,512	6,726	94,1	4,95	1,275
	BaFe ₁₂ O ₁₉	5,886	5,886	23,146	694,488	10,752	5,9		
0,2	La _{0.7} Ba _{0.3} MnO ₃	5,515	5,515	13,551	356,904	6,745	100	6,08	1,179
0,4	La _{0.7} Ba _{0.3} MnO ₃	5,538	5,538	13,500	358,593	7,044	90	6,94	2,184
	MnO	3,006	3,006	5,257	51,146	13,139	5,5		
	ZnO	3,245	3,245	5,198	47,413	17,394	4,5		
0,6	La _{0.7} Ba _{0.3} MnO ₃	5,535	5,535	13,516	358,668	7,164	80	7,80	2,500
	MnO	3,382	3,382	5,198	52,014	13,588	12,2		
	ZnO	3,245	3,245	5,197	47,409	17,396	7,8		

It is shown in Table 1 that the criteria-of-fit (Rwp) value and the goodness-of-fit (χ^2) value of the single phased lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.4}Zn_{0.2}Fe_{0.4})O_3$ ($x = 0.2$) is 6.08% and 1.179 respectively. The goodness-of-fit (χ^2) value of the single phased lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{0.4}Zn_{0.2}Fe_{0.4})O_3$ ($x = 0.2$) is below the allowed value of the referenced literature which is 1.3 [14]. The change of the lattice structure parameter on each sample compound shown that the injection of the ferrite ion (Fe^{+3}) and zinc ion (Zn^{+2}) into the manganese ion (Mn^{+2}) of the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ is successfully accomplished.

In addition, the single-phase sample that is formed can be used as the best material for electromagnetic wave absorber materials [15]. The presence of ferrite ion (Fe^{3+}) and zinc ion (Zn^{2+}) in the sample results in a mixed valence of manganese ions between Mn^{3+} and Mn^{4+} ions, causing magnetic interactions. Magnetic interactions occur double exchange and super exchange between Mn^{3+}/Mn^{3+} and Mn^{3+}/Mn^{4+} ions, respectively. As a result of this super exchange phenomenon, the sample can be used as an electromagnetic wave absorber [16].

3.2 Surface morphology analysis and compound compositions analysis

The surface morphology analysis result of the lanthanum manganite system of $(La_{0.8}Ba_{0.2})(Mn_{(1-x)/2}Zn_xFe_{(1-x)/2})O_3$ with injector concentration of $x = 0$, $x = 0.2$, $x = 0.4$ and $x = 0.6$ is shown in Figure 6.

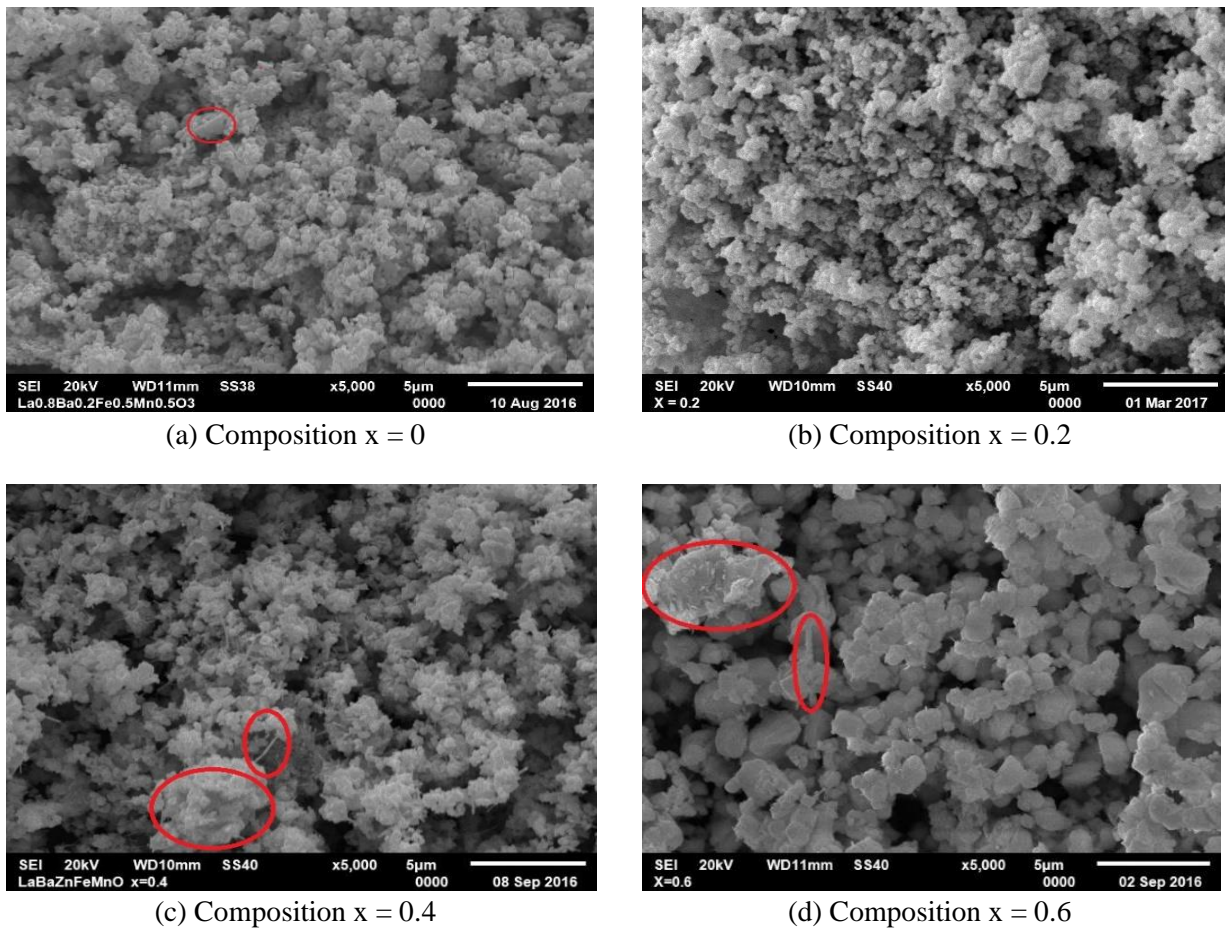


Figure 6. The surface morphology of the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$

It is shown in Figure 6 (a) that the surface morphology of the sample compound was an inhomogeneous sphere. It is in accordance with the phase analysis result that the sample compound has two phases. It is shown in Figure 6 (b) that the surface morphology of the sample compound was a homogeneous sphere. It is in accordance with the phase analysis result that the sample compound has single phase. It is shown in Figure 6 (c) and Figure 6 (d) that the surface morphology of the sample compounds was an inhomogeneous sphere with some clump visibly seen. These visibly seen clumps are assumed to be a different phase from the rest. It is in accordance with the phase analysis result that the sample compound has three phases.

The compound compositions analysis result of the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$ with injector concentration of $x = 0$, $x = 0.2$, $x = 0.4$ and $x = 0.6$ is shown in Table 2.

Table 2. The compound compositions analysis result of the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$

Sample (x)	Element	Mass (%)		Atom (%)	
		Observation	Calculation	Observation	Calculation
0	La	44,90	45,92	17,00	16
	Ba	12,13	11,35	4,64	4
	Fe	15,18	11,54	14,30	10
	Mn	11,72	11,35	11,22	10
	O	16,07	19,84	52,83	60
0.2	La	47,80	45,55	21,08	16
	Ba	11,59	11,25	5,17	4
	Zn	6,27	5,36	5,88	4
	Fe	12,42	9,16	13,62	8
	Mn	10,95	9,01	12,21	8
0.4	O	10,97	19,67	42,03	60
	La	47,01	45,18	22,91	16
	Ba	8,68	11,17	4,28	4
	Zn	20,37	10,63	21,09	8
	Fe	8,93	6,81	10,82	6
0.6	Mn	7,54	6,70	9,26	6
	O	7,47	19,51	31,60	60
	La	37,52	44,81	18,19	16
	Ba	21,65	11,08	10,62	4
	Zn	26,79	15,82	27,61	12
	Fe	2,75	4,50	3,33	4
	Mn	2,44	4,43	2,98	4
	O	8,85	19,36	37,27	60

It is shown in Table 2 that the compound composition of each sample compound is in accordance with the compound composition at the preparation stage. The mass fraction percentage and the atom fraction percentage are relatively equal for the observed and calculated portion. The atom fraction percentage of the manganese atom (Mn) and the ferrite atom (Fe) is decreased for sample with injector concentration of $x = 0.4$ and $x = 0.6$ while the zinc atom (Zn) is increased. It is caused by the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{(1-x)/2}\text{Zn}_x\text{Fe}_{(1-x)/2})\text{O}_3$ used.

4. Conclusions

The conclusion based on this research is as follow. The lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$ ($x = 0.2$) is the most suitable compound to be considered for an electromagnetic waves absorbing material based application. The refinement pattern result of the x-ray powder diffraction method (XRD) shown that a single phase was occurred in the sample compound of the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$. It has trigonal lattice crystal structure of (r-3c) point group with lattice parameter of $a = b = 5.5147 \text{ \AA}$ and $c = 13.5507 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, a volume unit cell of $V = 356.904 \text{ \AA}^3$ and a density of $\rho = 6.745 \text{ g.cm}^{-3}$. The scanning electron microscopy (SEM) result shown that the surface morphology of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$ has a homogeneous sphere structure with compound composition relatively homogeneous. The XRD and SEM structure analysis result of the lanthanum manganite system of $(\text{La}_{0.8}\text{Ba}_{0.2})(\text{Mn}_{0.4}\text{Zn}_{0.2}\text{Fe}_{0.4})\text{O}_3$ shown that the compound is feasible for further studied.

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