

Effect of Manganese Addition on the Structure, Magnetic Properties and Microwave Absorption of $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{1/2(1-x)}\text{Ti}_{1/2(1-x)}\text{O}_3$

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Abstract. We have carried out modification of $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{\frac{1}{2}(1-x)}\text{Ti}_{\frac{1}{2}(1-x)}\text{O}_3$ ($x = 0.1 - 0.8$) magnetic materials by wet milling method. Raw materials of La_2O_3 , BaCO_3 , Fe_2O_3 , TiO_2 and MnCO_3 were mixed according to stoichiometry calculation for each composition. The mixture was milled for 5 hours and then sintered at 1000 °C for 5 hours. The refinement results by X-ray diffraction pattern shows that the increasing Mn composition enhances the mass fraction of $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{\frac{1}{2}(1-x)}\text{Ti}_{\frac{1}{2}(1-x)}\text{O}_3$ phase which has the same structure as LaMnO_3 . For $x = 0.8$ a single phase of LaMnO_3 was formed. The single phase has a crystal monoclinic crystal structure with space group of $I 1 2 / a 1$, with lattice parameters given by $a = 5.519(5) \text{ \AA}$, $b = 5.5537(5) \text{ \AA}$ and $c = 7.8176(9) \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 90.345(6)^\circ$, $V = 239.64(3) \text{ \AA}^3$, $\rho = 6.463 \text{ gr.cm}^{-3}$, $wRp = 5.96$, and χ^2 (chi-squared) = 1.17. The hysteresis curve shows that the sample with composition $x = 0.8$ produces ferromagnetic behaviour at room temperature. The ferromagnetic properties arise due to the mixed valence of Mn^{3+} and Mn^{4+} ions through a double exchange mechanism. The results of the microwave absorption indicated that there was a broadening of absorption peak frequency at 9.9 GHz. The reflection loss (RL) increases with the increasing of LaMnO_3 phase. For $x = 0.8$ we have the best of RL where the microwave absorption was calculated reaching 95% at the highest peak frequency with a thickness of 1.5 mm. Thus we have been successful in creating a single phase of $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{\frac{1}{2}(1-x)}\text{Ti}_{\frac{1}{2}(1-x)}\text{O}_3$ with application as a microwave absorber.

Keywords: Perovskite, $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{\frac{1}{2}(1-x)}\text{Ti}_{\frac{1}{2}(1-x)}\text{O}_3$, composition, phase, ferromagnetic, microwave absorber

1. Introduction

One research topic which attracts great interest nowadays is a material that can absorb microwaves with applications in the field of electronics, telecommunications and defense. There are two important factors that must be met so that the material can absorb microwaves, namely that the material should have magnetic loss (component permeability) and dielectric loss (permittivity component) is high [1].

Recently, some of the magnetic material successfully demonstrated absorption in the microwave region. The magnetic material is hexa-ferrite system [2-5] which has proven capable of absorbing microwave because they have high permeability values. Meanwhile other interesting magnetic



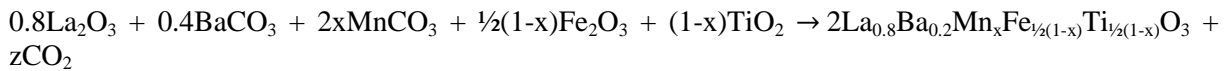
material called perovskite ABO_3 are manganite-based [6-9] because they have a high permittivity value has also attracted lots of interest.

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 $La_{0.8}Ba_{0.2}MnO_3$ 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 $La_{0.8}Ba_{0.2}MnO_3$ measured at room temperature has a nonlinear magnetic pattern as a function the applied magnetic field [10].

In this study, we will present structural engineering materials called perovskite $La_{0.8}Ba_{0.2}MnO_3$, where the element manganese is substituted with iron (Fe) to increase its permeability and titanium (Ti) to increase the permittivity in the material. The focus of discussion is to determine the material structure, magnetic properties and electromagnetic wave absorption capability due to addition of manganese and titanium.

2. Material and Method

The raw materials used were lanthanum oxide (La_2O_3), barium carbonate ($BaCO_3$), manganese carbonate ($MnCO_3$), iron oxide (Fe_2O_3), and titanium dioxide (TiO_2) from Merck product with high purity. Each of raw materials was weighed suitable with the compositions stoichiometry as x function ($x = 0 - 0.8$) according to reaction as follows:



The samples consist of eight compositions, namely, $La_{0.8}Ba_{0.2}Mn_{0.1}Fe_{0.45}Ti_{0.45}O_3$, $La_{0.8}Ba_{0.2}Mn_{0.2}Fe_{0.4}Ti_{0.4}O_3$, $La_{0.8}Ba_{0.2}Mn_{0.3}Fe_{0.35}Ti_{0.35}O_3$, $La_{0.8}Ba_{0.2}Mn_{0.4}Fe_{0.3}Ti_{0.3}O_3$, $La_{0.8}Ba_{0.2}Mn_{0.5}Fe_{0.25}Ti_{0.25}O_3$, $La_{0.8}Ba_{0.2}Mn_{0.6}Fe_{0.2}Ti_{0.2}O_3$, $La_{0.8}Ba_{0.2}Mn_{0.7}Fe_{0.15}Ti_{0.15}O_3$, and $La_{0.8}Ba_{0.2}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_3$ furthermore are respective called by $x = 0.1$, $x = 0.2$, $x = 0.3$, $x = 0.4$, $x = 0.5$, $x = 0.6$, $x = 0.7$, and $x = 0.8$. Methods used are a solid state reaction use mechanical milling technique of wet. This method is simple and inexpensive. The each of mixtures were milled by HEM (high energy milling SPEX8000 mixer/mil) for 5 hours and dried in oven at $100\text{ }^\circ\text{C}$ for 5 hours. The samples made were sintered in Furnace at $1000\text{ }^\circ\text{C}$ for 5 hours, and then the each of samples were characterized by using X-ray diffraction (XRD) to know phases formed.

The samples with compositions selected were characterized furthermore by using scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), particle size analyzer (PSA), vibrating simple magnetometer (VSM), and vector network analyzer (VNA) respective to know morphology of particle, elemental composition analysis, distribution of particle size, magnetic properties, and performance of microwave absorption. Especially for the phase qualitative and quantitative of analysis were carried out using Rietveld method with applying GSAS program [11].

3. Results and Discussions

Figure 1 shows X-ray diffraction profiles of synthesized material which respective profiles of system $La_{0.8}Ba_{0.2}Mn_xFe_{\frac{1}{2}(1-x)}Ti_{\frac{1}{2}(1-x)}O_3$ ($x = 0.1 - 0.8$) are compared.

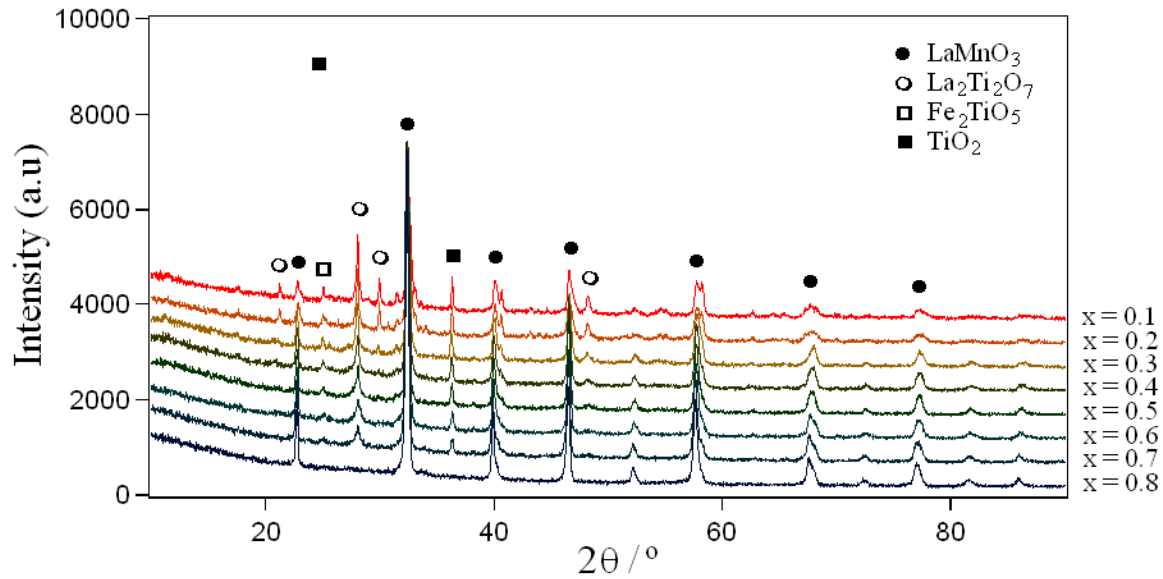


Figure 1. X-ray diffraction profile of magnetic system $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{1/2(1-x)}\text{Ti}_{1/2(1-x)}\text{O}_3$.

The results of phase identification shows that sample with composition $x = 0.1$ consists of four phases, namely phase of LaMnO_3 (COD : 1001820), $\text{La}_2\text{Ti}_2\text{O}_7$ (COD: 2002196), Fe_2TiO_5 (COD: 2002318), and TiO_2 (COD: 9015662). In this composition appears that the substitution of Fe and Ti excess caused a reaction becomes imperfect so that Fe and Ti atoms form another phase. Samples with composition $x = 0.2 - 0.4$ appears that phase of LaMnO_3 increased while others decreased. Fe_2TiO_5 phase to be lost on the composition $x = 0.5$, so that the sample only consists of three phases. Phase of LaMnO_3 growing increases with increasing manganese in the sample composition and phase $\text{La}_2\text{Ti}_2\text{O}_7$ and TiO_2 are getting down (composition $x = 0.6 - 0.7$) and disappeared on the composition $x = 0.8$. Single phase of LaMnO_3 obtained when the composition $x = 0.8$. Thus the change in the number of phases which are formed on the composition $x = 0.1$, $x = 0.5$ and $x = 0.8$.

Results refinement X-ray diffraction pattern and morphology of particle for a third of the composition is shown in figure 2. While the crystal structure parameters and mass fraction of phase formed is shown in table 1.

Table 1. The value of structure parameters, criteria of fit (R_{wp}), goodness of fit (χ^2) and the mass fraction of phase formed with variations in composition.

| Sample (x) | Phase | Lattice parameter (Å) | | | V (Å ³) | ρ (g/cm ³) | Fraction wt% | R_{wp} (%) | χ^2 |
|---------------|------------------------------------|-----------------------|-----------|-----------|------------------------|--------------------------------|-----------------|-----------------|----------|
| | | a | b | c | | | | | |
| 0.1 | LaMnO_3 | 5.525(1) | 5.536(1) | 7.769(1) | 237.6(1) | 6.518 | 42.66 | 9.20 | 1.41 |
| | $\text{La}_2\text{Ti}_2\text{O}_7$ | 25.571(7) | 7.812(3) | 5.584(3) | 1115.6(8) | 5.782 | 45.21 | | |
| | Fe_2TiO_5 | 3.780(5) | 11.432(1) | 9.505(5) | 410.7(3) | 3.745 | 2.92 | | |
| | TiO_2 | 4.508(1) | 4.508(1) | 2.964(1) | 60.24(6) | 4.403 | 9.21 | | |
| 0.5 | LaMnO_3 | 5.5038(7) | 5.5427(7) | 7.8074(9) | 238.17(4) | 6.503 | 69.45 | 7.30 | 1.27 |
| | $\text{La}_2\text{Ti}_2\text{O}_7$ | 25.605(1) | 5.031(1) | 13.695(7) | 1134.0(2) | 5.694 | 24.08 | | |
| | TiO_2 | 4.496(2) | 4.496(2) | 2.965(1) | 59.97(7) | 4.424 | 6.46 | | |
| 0.8 | LaMnO_3 | 5.519(5) | 5.5537(5) | 7.8176(9) | 239.64(3) | 6.463 | 100.00 | 5.96 | 1.17 |

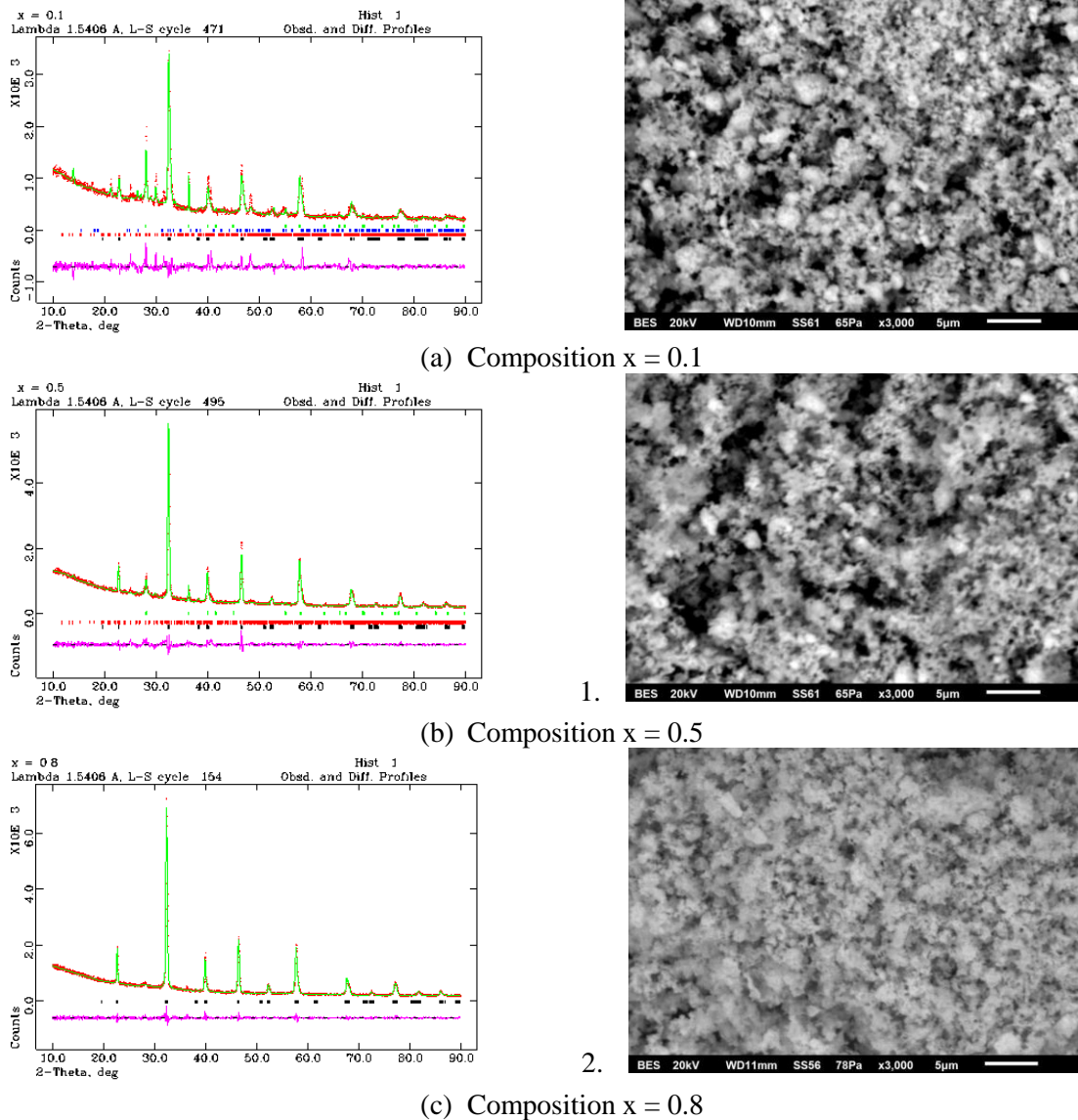


Figure 2. Refinement result of XRD and SEM image on the $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{1/2(1-x)}\text{Ti}_{1/2(1-x)}\text{O}_3$.

Figure 2 and table 1 shows a correlation between the phases formed and the morphology of the particles of each composition. In composition $x = 1$ and $x = 0.5$ has been shown that the samples consist of multi-phase and is supported by the results of particle morphology is very diverse. While the composition $x = 0.8$, sample is single-phase so that it seemed at the SEM image shown morphology uniform and homogeneous across the surface. Single phase of system $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{1/2(1-x)}\text{Ti}_{1/2(1-x)}\text{O}_3$ particles were successfully synthesized by solid state method appears at the manganese composition of $x = 0.8$.

In addition, the hysteresis curve shows that the sample is ferromagnetic behavior as shown figure 2. The ferromagnetic behavior for the samples because the presence of mix valence from manganese ions between Mn^{3+} and Mn^{4+} ions, giving rise magnetic interactions. The magnetic interactions are due double exchange and superexchange which occur respective between $\text{Mn}^{3+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions [10].

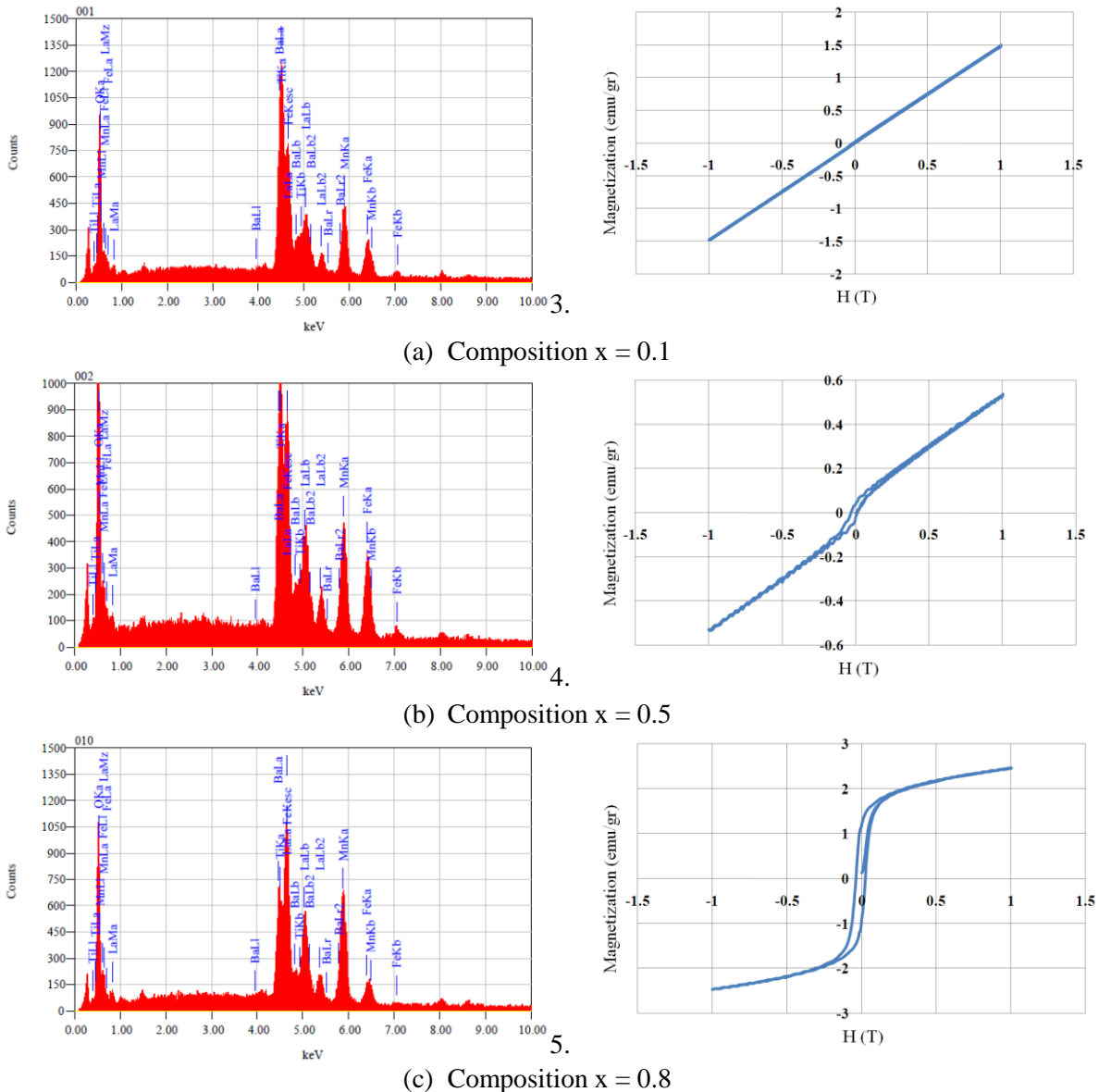


Figure 3. The element analysis and magnetic properties on the $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{1/2(1-x)}\text{Ti}_{1/2(1-x)}\text{O}_3$.

In figure 3 is shown that the magnetic properties of the composition $x = 0.1$ is paramagnetic because the content of Mn in the composition is so low so that the LaMnO_3 phase is relatively small as shown in figure 4. Then in the composition $x = 0.5$, Mn content greater so present ferromagnetic properties of materials this is because the mass fraction of LaMnO_3 phase greater. While the composition $x = 0.8$ magnetic properties change into ferromagnetic because the composition is already forming a single phase of LaMnO_3 .

The ferromagnetic properties of system $\text{La}_{0.8}\text{Ba}_{0.2}\text{Mn}_x\text{Fe}_{1/2(1-x)}\text{Ti}_{1/2(1-x)}\text{O}_3$ depends on the presence of Mn ions with different valence (mixed-valence). The presence of Mn^{3+} and Mn^{4+} is closely linked with ferromagnetic behavior to this system where this phenomenon can be explained by the double-exchange theory of Zener [12]. Mn^{3+} ion has the electron configuration $3d^4$, so that the orbital t_{2g} fully charged while there is a single electron spin in orbital e_g . However Mn^{4+} ion has the electron configuration $3d^3$ in which the orbital t_{2g} also

fully charged while the e_g orbital empty. Therefore, the electron spin configuration Mn^{3+} is able to hop to fill the void in the configuration Mn^{4+} through the intermediation anion O^{2-} without changing the direction of their spin.

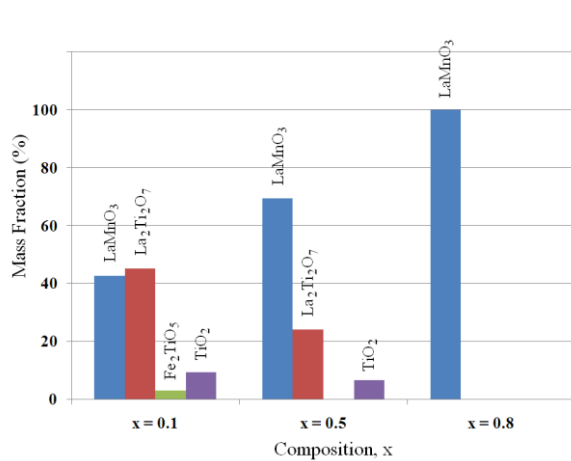


Figure 4. Mass fraction of phase formed.

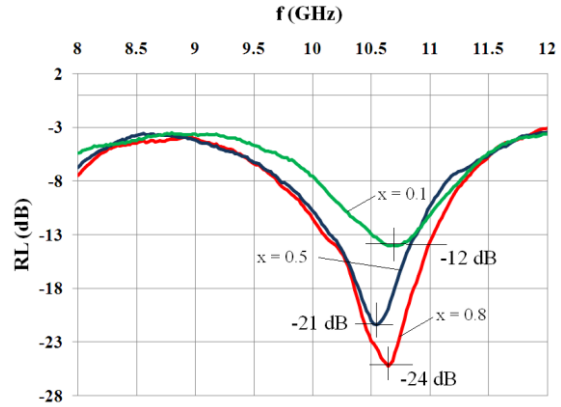


Figure 5. Reflection loss of the samples.

Measurement results of VNA shows that there are one of absorption peaks with reflection loss values of higher at range frequency of 8 – 12 GHz as shown figure 5. It appears that the greater the mass fraction of $LaMnO_3$ phase formed the larger RL possessed by the material. This indicates that the manganese composition of $x = 0.8$ has the best of microwave absorbing properties in the frequency range of 8- 12 GHz, whose value of the absorbing peaks are -24 dB at 10.5 GHz. The study concluded that a single phase $La_{0.8}Ba_{0.2}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_3$ material has been successfully synthesized showing a good candidate as microwave absorbing materials.

4. Summary

Single phase of system $La_{0.8}Ba_{0.2}Mn_xFe_{\frac{1}{2}(1-x)}Ti_{\frac{1}{2}(1-x)}O_3$ particles were successfully synthesized by solid state method. The refinement of x-ray diffraction for the manganese composition of $x = 0.8$ has been confirmed a single phase. The hysteresis curve shows that the sample with the composition of $x = 0.8$ is ferromagnetic behavior at room temperature. The ferromagnetic properties arise because of the mixed valence of Mn^{3+} and Mn^{4+} ions through a double exchange of mechanism. The manganese composition of $x = 0.8$ has the best of microwave absorbing properties in the frequency range of 8- 12 GHz, whose value of the absorbing peaks are -24 dB at 10.5 GHz.

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