

Structural and Absorption Characteristics of Mn-Ti Substituted Ba-Sr Hexaferrite Synthesized by Mechanical Alloying Route

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ABSTRACT

The synthesis and characterization of composition $(Ba,Sr)O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0; 0.25; and 0.5) compound by using solid state reaction have been performed. The raw materials were BaCO₃, SrCO₃, Fe₂O₃, MnCO₃, and TiO₂. The mixed powder was compacted at 5000 psi into pellets and sintered at 1050°C in the air at atmosphere pressure for 15 hour and furnace cooling. X-ray diffraction studies indicate expansion of hexagonal unit cell and compression of atomic density with substitution of Mn²⁺ and Ti⁴⁺ ions. The substitution increases density and intergrain connectivity in the microstructure of sintered samples. Effect of substitution upon magnetic properties revealed that total magnetization, remanence and coercivity changed with substitution due to preferential site occupancy of substituted Mn²⁺ and Ti⁴⁺ ions. Since the coercivity and total magnetization may be controlled by substitution while maintaining resistive properties, making this material useful for microwave absorber.

KEYWORDS: Barium hexaferrite, solid state, substitution, crystal structure, microstructure, magnetic properties, microwave absorber

1. INTRODUCTION

Much research works have been paid to the ceramic magnetic compound based on Barium and strontium hexaferrites with a chemical formula of respectively $BaO.6Fe_2O_3$ and $SrO.6Fe_2O_3$. Compared with other ferrite compounds, Ba and Sr hexa ferrites have a much larger uniaxial anisotropy constant and high saturation magnetisation values and hence potential for permanent magnet applications^[1-6]. In addition, since the compounds are made of oxide based materials and hence a much larger resistivity value than other permanent magnets, ferrites are credited to another area of technological application like electromagnetic wave suppression or electromagnetic wave absorbtion especially at high frequencies range like Radar Absorbing Material^[7-10]. However, the latter requires substitution of Fe^{3+} cations by suitable pairs of cations with a fixed ratio to maintaining the average 3+ valence state.

There have been many reports on cationic substitution of M-type hexa ferrites for microwave absorber materials. Induced magnetic anisotropy of single crystal Co-Ti substituted Barium hexaferrite was shown changing considerably from $K_1 = 5.38 \times 10^5$ erg.g⁻¹ for undoped Ba-haxaferrite to as low as 0.65 x 10⁵ erg.g⁻¹ at a substitution rate x = 0.8 ^[11]. At even higher substitution rate (x = 1.1) uniaxial magnetocystalline anisotropy changed to planar anisotropy. Reduction in anisotropy constant of permanent magnet materials like Ba,Sr hexaferrite is primarly required since a substantially low coercivity while the magnetisation remains high are the most properties that required for microwave absorber applications.

The effect of fine particle size especially in nano size regime are well known to affect both remanence and coercivity in permanent magnets^[12-14]. Exchanged grain interactions of neighbouring gain were shown responsible to reduce substantially coercivity following the reduction of anisotropy constant. In the present work, we report a structural change of Mn^{+2}/Ti^{+4} substituted Ba,Sr hexaferrite derived from X-Ray Diffraction traces and structure Rietveld Analysis. The corresponding coercivity were evaluated by means of vibrating sample magnetometer (VSM) and microwave absorbing characteristics were studied in the frequency range between 8 and 20 GHz. The materials under investigation are a series of Barium-strontium hexaferrite with $(Ba,Sr)O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0; 0.25; and 0.5) compositions obtained from mechanical alloying. Extended milling time was applied to derive nanocrystalline materials.

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2. MATERIALS AND METHODS

The samples of composition $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0; 0.25; and 0.5) were synthesized by solid state reaction. The starting raw materials were BaCO₃, SrCO₃, Fe₂O₃, MnCO₃, and TiO₂ with a purity > 98%. The chemical reaction of the compound formation process of $(Ba,Sr)O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ can be described as follows:

BaCO₃ + SrCO₃ + 12(1-x)Fe₂O₃ + 2xMnCO₃ + 2xTiO₂ → $2Ba_{0.5}Sr_{0.5}O.6Fe_{2(1-x)}Mn_xTi_xO_3 + yCO_2 + zO_2$

The ingredients were mixed in stoichiometric proportion, and ball milling process was carried out in a vibratory mill type SPEX 8000 CertiPrep Mixer/Mill for 10 hours under air atmosphere. The weight ratio of balls to milled material was 5:1. The mill generated vibrations of the balls and the material inside the container. The finely mixed powder was compacted at 5000 psi into pellets and sintered in the electric chamber furnace THERMOLYNE at 1050°C in the air at atmosphere pressure for 15 hour and furnace cooled.

The qualitative and quantitative of analysis were carried out using the PW1710 Philips diffractometer equipped with a tube provided with cobalt anode. It was supplied by current of 30 mA and voltage of 40 kV. The length of radiation (CoK \Box) was 1.7890 Å. The data of diffraction angles range from 20° to 80° and 0.02° step. The Rietveld analysis was performed applying GSAS program. The pseudo-Voigt function was used in the describing of diffraction line profiles at Rietveld refinement. The magnetic hysteresis loops of obtained powder material were measured by the Vibrating Sample Magnetometer (VSM). The surface morphology and element identification of the sample were analyzed by using the JEOL scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively. The reflection and transmission of microwave were carried out using the *Vector Network Analyzer* Tipe ADVANTEST R3770 with test range of frequency from 5 GHz until 18 GHz. The sample was prepared into pellet with diameter and thickness are 25 mm and 2 mm, respectively.

3. RESULTS AND DISCUSSION

Hexagonal barium ferrites having the chemical formula of BaO.6Fe₂O₃ are well known hard magnetic materials, which are based on iron oxide. Barium ferrite possesses relatively high Curie temperature (*Tc*), great coercive force (*Hc*) and high magnetic anisotropy field (*Ha*). They are also as well as its excellent chemical stability and corrosion resistivity. Substitution for the Sr²⁺ is an effective method to vary the magnetic properties of Barium ferrite. After the Sr ion is substituted with Ba become (Ba,Sr)O.6Fe₂O₃, the magnetic properties of barium strontium ferrite are changed. The magnetic properties of (Ba,Sr)O.6Fe₂O₃ need modified in order to applicable in microwave devices, electromagnetic shielding fields, or electromagnetic wave absorber. Furthermore, it is important to understand the origin of the property changes when these substitutions are made. Because of their high values of magnetization (M) and low coercive force (*Hc*), hexaferrites are important for electromagnetic wave absorber applications, through appropriate cationic substitution for some of the Fe³⁺ ions with Mn²⁺ and Ti⁴⁺ in (Ba,Sr)O.6Fe₂O₃. The formulations reported here are made of a single phase Mn-Ti substituted (Ba,Sr)O.6Fe₂O₃. The choice of Ti⁴⁺ ion substitution is made to reduce a part of Fe³⁺ to Fe²⁺.

3.1. X-ray diffraction

Figure 1 shows the XRD patterns of the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ sample under the varied x values (x = 0; 0.25; and 0.5). The characterized peaks are as expected and in general similar with those published in a standard refference. Phase identification based on the refinements of the XRD pattern confirmed the formation of SrO.6Fe₂O₃ phase. With respect to the position of diffraction lines and their relative intensities, the synthesized (Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3 (x = 0), (Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3 (x = 0.25), and (Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3 (x = 0.5) obtained from the present study demonstrated characteristic peaks consistent with SrO.6Fe₂O₃.



Figure 1. The XRD patterns of the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0; 0.25; and 0.5).

According to the Hanawalt table it is showed that the results obtained can be identified as the $SrO.6Fe_2O_3$ single phase. Since the Hanawalt table only can be used to qualitative analysis of each compounds, rietan's code (GSAS/RIETAN) is used for quantitative measurement.

3.2. Scanning electron microscope and Energy dispersive spectroscopy

Figure 2 show the microstructures of $(Ba,Sr)O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ samples under the varied *x* values (*x* = 0; 0.25; and 0.5). The microstructure analyses show that the particle shapes are polygonal with the varied particle sizes of 2 ~ 5 \Box m distributed homogeneously on the surface of the samples.



Figure 2. The microstructures of $(Ba,Sr)O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ samples (x = 0; 0.25; and 0.5).

The element identification were analyzed by using energy dispersive spectroscopy (EDS) of samples is shown in Figure 3 and Table 1.



Figure 3. The element identification of the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0; 0.25; and 0.5).

T	Table 1.	The element	identification were analyzed by using energy dispersive spectroscopy	
	No.	Element	(Ba,Sr) _{0.5} O.6Fe _{2(1-x)} (Mn,Ti) _x O ₃	
			r = 0 $r = 0.25$	$\mathbf{r} = 0$

	Liement	(Da;01)0,50:01 (2(1-x)(1011,11)x05					
		<i>x</i> =	= 0	<i>x</i> = 0.25		<i>x</i> = 0.5	
		wt%	at%	wt%	at%	wt%	at%
1.	Ba	6.61	1.62	7.63	1.83	7.63	1.81
2.	Sr	4.32	1.65	4.22	1.59	3.53	1.31
3.	Fe	60.17	36.14	45.63	26.99	30.66	17.88
4.	Mn	-	-	7.04	4.23	12.50	9.19
5.	Ti	-	-	5.75	3.97	12.60	8.57
6.	0	28.90	60.59	29.74	61.39	30.08	61.24

3.3. Rietveld analysis

The space group of BaO.6Fe₂O₃ crystal structure is P 63/m m c (Vol. I, 194), hexagonal crystalline with lattice parameter of a = b = 5.8821 Å, and c = 23.0230 Å with the $\Box = \Box = 90^{\circ}$ and $\Box = 120^{\circ}$. The Wyckoff position or number of equivalent points per unit cell according to the Obradors research result^[15].

Figure 4 shows the XRD pattern refinement result of the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0) sample. The quality of fitting of R (criteria of fit) and χ^2 (goodness of fit) factors were in minimum values; the allowed χ^2 (chi-squared) factor value is as high as 1.3.



And Figure 5 shows the XRD pattern refinement result of the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0.25) sample.



Parameter of statistic χ^2 (chi-squared) = 1.3, wRp = 3.58, and Rp = 2.82

While Figure 6 shows the XRD pattern refinement result of the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ (x = 0.5) sample.



Parameter of statistic χ^2 (chi-squared) = 1.3, wRp = 2.94, and Rp = 2.31

Fig. 4, Fig. 5, and Fig. 6 show the fitting curve for the $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ samples for x = 0, x = 0.25, and x = 0.5, respectively. The plus symbol (+) represents the observation, line symbol (-) represents the calculation, Miller index is represented by bar symbol (I) and the difference between observation and calculation is represented by line symbol (-). The difference between the two curves indicates the quality of fitting method, namely the over straight of the line the quality of fitting is good and in accordance to the standard reference of the sample.

Fig. 4, Fig. 5, and Fig. 6 showed that all profiles are in good agreement among the observation and calculations. This can be seen from the small number of *R* and χ^2 (chi-squared) factors. It can be concluded that all of the refinement works are well fitted to the original data for the (Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO₃ samples under the varied *x* values (*x* = 0; 0.25; and 0.5). And the cationic distribution in (Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO₃ (x = 0.25 and x = 0.5) was showed in Table 2.

Referring to EDS and XRD result, a single phase Mn-Ti substituted (Ba,Sr)_{0.5}O.6Fe₂O₃ have been made successfully.

	Table 2. Cationic distribution in	$(Ba,Sr)_{0.5}O.6Fe_{2(1-1)}$	$_{x}(Mn,Ti)_{x}O_{3}$ (x = 0.25	5 and $x = 0.5$) observed	by x-ray diffraction
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Atom Site Point			Cationic distribution						
		Symmetry	(Ba,Sr) _{0.5} O.6Fe _{2(1-x)} (Mn,Ti) _x O ₃		,Ti) _x O ₃	(Ba,Sr) _{0.5} O.6Fe _{2(1-x)} (Mn,Ti) _x O ₃			
			(x = 0.25)				(x = 0.5)		
			Fe	Ti	Mn	Fe	Ti	Mn	
Fe ⁽¹⁾	2a	3m	0.79	0.14	0.07	0.47	0.28	0.25	
			(79 %)	(14 %)	(7%)	(47 %)	(28 %)	(25 %)	
Fe ⁽²⁾	2b	3m	0.96	0.04	-	0.82	0.13	0.05	
			(96 %)	(4 %)	-	(82 %)	(13 %)	(5%)	
Fe ⁽³⁾	4f1	3m	1.46	0.28	0.25	1.05	0.49	0.46	
			(73 %)	(14 %)	(13 %)	(52 %)	(25 %)	(23 %)	
Fe ⁽⁴⁾	4f2	3m	1.37	0.31	0.32	1.05	0.45	0.49	
			(69 %)	(15 %)	(16 %)	(52 %)	(23 %)	(25 %)	
Fe ⁽⁵⁾	12k	m	4.10	0.95	0.94	2.76	1.61	1.62	
			(68 %)	(16 %)	(16 %)	(46 %)	(27 %)	(27 %)	
E	lementer	analysis	$Ba_{0.58}Sr_{0.51}Fe_{8.64}Mn_{1.35}Ti_{1.28}O_{19.64}$			Ba_{0.57}Sr_{0.42}Fe_{5.72}Mn_{2.94}Ti_{2.76}O_{19.59}			
Sti	ructure re	finement	Ba _{0.5} Sr _{0.5} Fe _{8.68} Mn _{1.72} Ti _{1.58} O ₁₉			Ba _{0.5} Sr _{0.5} Fe _{6.15} Mn _{2.96} Ti _{2.87} O ₁₉			

While the effect of the doping of Mn^{2+} and Ti^{4+} ions on crystal structure is obtained the cell parameter and volume of unit cell changed as shown in Fig. 7. From XRD refinement result can be concluded, that the cell parameter and volume of unit cell increases while the atomic density decrease with increasing doping of Mn^{2+} and Ti^{4+} ions.



3.4. Magnetization

The hysteresis loops in Fig. 8 for $(Ba,Sr)O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ samples (x = 0; 0.25; and 0.5), and show the magnetic data and summarized in Table 3.

The hysteresis loop consists of intrinsic saturation Ms, remanence Mr, and coercivity Hc. This saturation is the state when the material cannot absorb a stronger magnetic field such that an increase of magnetization force produces no significant change in magnetic flux density. The remanence Mr, for the samples shows the magnetization left behind in a medium after the external magnetic field has been removed. And coercivity also called the coercive force of a material is equal to the demagnetizing force required to reduce residual induction to zero in a magnetic field after magnetizing to saturation.



Magnetic Field, H (kOe)

Figure 8. Hysteresis loops of $(Ba,Sr)_{0.5}O.6Fe_{2(1-x)}(Mn,Ti)_xO_3$ samples (x = 0; 0.25; and 0.5).

Figure 8 appear that magnetic characterization show that the coercivity for x = 0 was 1508 Oe decrease drastically to 256 Oe for x = 0.5. In other hand that the coercivity decrease with increase in Mn and Ti concentration. This effect is related with Fe³⁺ magnetic moment change after they have already substituted Mn²⁺ and Ti⁴⁺ ions.

No.	Sample	Remanence, Mr (emu.gr ⁻¹)	Saturation, Ms (emu.gr ⁻¹)	Coercivity, Hc (Oe)
1.	x = 0	37.58	59.29	1508
2.	<i>x</i> = 0.25	24.46	58.70	557
3.	x = 0.5	7.58	21.94	256

Table 3. Summary of magnetization measurement for samples

3.5. Absorption properties

Apart from other application, substituted hexagonal are very promising materials in the domain of electromagnetic wave a absorber and expected to show better performances at high frequency (> 1 GHz) compared to spinel compounds in the same frequency band. Fig. 9 was showed the variation of reflection loss versus frequency, which was observed in the samples.

It clearly appears that the bandwidth that can be covered by this ferrite is more than 9 GHz with reflection loss higher than -30 dB. The maximum reflection loss of this band is -30 dB at matching frequency at 13.5 GHz. This dispersion is due the domain wall motion at lower frequency and spin resonance at higher frequency, respectively.



Figure 9. Curve reflection loss sample x = 0.0, x = 0.25 and x = 0.

4. Conclusions

From the research result can be concluded, that the effect of the doping of Mn^{2+} and Ti^{4+} ions on crystal structure is obtained the cell parameter and volume of unit cell changed. The microstructure analyses show that the particle shapes are polygonal with the varied particle sizes of $2 \sim 5 \square m$ distributed homogeneously on the surface of the samples. The coercivity decreases with increase in Mn and Ti concentration. This effect is related with Fe³⁺ magnetic moment change after they have already substituted Mn²⁺ and Ti⁴⁺ ions.

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