SYNTHESIS AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE Ba₃Co_{2 (0.8-x)}Mn_{0.4}Ni_{2x}Fe₂₄O₄₁PREPARED BY CITRATE SOL-GEL METHOD

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The synthesis of nanocrystalline Z-type hexaferrites Ba₃ Co_{2 (0.8-x)} Mn_{0.4} Ni_{2x} Fe₂₄ O₄₁

powders by citrate sol-gel method has been investigated. The effect of Mn²⁺ Ni²⁺ substitution on microwave absorption has been studied for Co-Z, where x varies from 0 to 0.15 in steps of 0.05, in frequency range from 12 to 20 GHz. X- ray diffraction (XRD), Mössbauer spectroscopy, vibrating sample magnetometry (VSM), transmission electron microscope (TEM), electron diffraction and vector network analyzer were used to analyze the structures electromagnetic and microwave absorption properties. The results showed that the addition x , leads to decreasing coercive force (H_c) and saturation magnetization.

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1. Introduction

With the rapid development of electric technology towards higher frequencies, there is an increasing demand for various chip components and hyper-frequency devices. Multi-Layer Chip Inductors (MLCI) are among the three most important passive components and some have attracted a lot of attention because of their application in anti-electromagnetic interference.

Traditional materials for making MLCI, such as the NiCuZn ferrite, cannot be used in hyper-frequency ranges, since the cut-off frequency is limited below 100 MHZ by their spinel structure. On the other hand, hexagonal ferrites have a much higher cut-off frequency than spinel ferrites, owing to their planar magneto-crystalline anisotropy.

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Hexagonal ferrites constitute a large class of ferromagnetic oxides that were first synthesized in 1950s, at the Philips Laboratories[1]. Polycrystalline hexaferrites, in particular, are very useful for microwave applications due to their very low dielectric loss. Hexagonal ferrites

are divided into six different types: $M(AFe_{12}O_{19})$, $W(AM_2Fe_{16}O_{27})$,

 $X(A_{2}Me_{2}Fe_{28}O_{46}), Y(A_{2}Me_{2}Fe_{12}O_{22}), U(A_{4}Me_{2}Fe_{36}O_{60}), Z(A_{3}Me_{2}Fe_{24}O_{41}), where Contract A = 0$

A = Ba, Sr, La and M = a divalent transition metal[2,3].

These compounds are prepared by using various synthesis routes such as chemical coprecipitation[4,5], low-temperature combustion[6], sol-gel[7], mechanical alloying[8,9], mechanical activation[10], solid-state reaction[11] and microemulsion and reverse microemulsion[12].

The Z-type Ba-ferrite, in particular, belongs to a family of planar hexagonal ferrites with high permeability, even in the GHz frequency range, and is an important soft magnetic material devices. Α member of this family for noise absorbent typical is Co 2 Z(Ba 3 Co 2 Fe 24 O 41), one of the most important microwave ferrites, with high permeability and low loss in hyper-frequency ranges. The saturation magnetization is 51 emu/g at room temperature (RT) and the Curie temperature is 690 K. At RT, Co₂Z has c-plane anisotropy with a large out-of-plane anisotropy field H_{θ} of 12 kOe and a small in-plane anisotropy field H_{ϕ} of about 0.12 kOe[13].

CoZ-type hexaferrites have also been prepared by several specific routes, each one resulting in samples with different properties.

Up to now,numerous papers have been published on the studies of Mössbauer spectra and microwave absorption for M- and W-type barium ferrites. However, only few considered the hyperfine and microwave absorption properties for Z-type barium ferrites [13,14].

In this paper, we report the structural, magnetic, hyperfine and microwave absorption properties for the Ba₃Co_{2 (0.8-x)}Mn_{0.4}Ni_{2x}Fe₂₄O₄₁ hexaferrite synthesized by a chemical method followed by heat treatment.

2. Experimental procedures

The samples were prepared, first, by the citrate sol-gel method. The starting materials used were Ba(NO₃)₂, Fe(NO₃)₃.9H₂O, Co(NO₃)₂.6H₂O, Mn(NO₃)₂, Ni(NO₃)₂.6H₂O, and citric acid. In a typical procedure for the Ba₃Co_{2 (0.8-x)}Mn_{0.4}Ni_{2x} Fe₂₄O₄₁ preparation (with X = 0, 0.05, 0.1 and 0.15), initially, stoichiometric amount of nitrates were dissolved in distilled water. Then, a stoichiometric amount of citric acid solution was added to the salt solution. In this method, the molar ratio of Ba:Fe was taken as 1:11.The molar ratios of citric acid to metal ions used were 1:1. The pH of the solution was adjusted to 6.0 using ammonia. Further, the solution was evaporated at 80 °C for 3 h and then heated at 100 °C to produce a dry gel. Finally, the dry gel was calcined at 1150 °C for 2h.

The composite specimens were prepared by mixing doped Co-Z ferrites and PVC powder with concentration of 80:20 by weight. Mixture of ferrite powders with PVC were plasticized and fired at 220° C and 5.5MPa. The pressed composites were in the form of cylindrical with different thicknesses and the diameter of 40 mm. The reflection loss of the absorbers were calculated from the SWR (standing-wave-ratio) measured as a function of frequency in the configuration shown in Fig. 1 using microwave Network Analyzer (R&S-ZVK). The network analyzer was fully calibrated before use.



Fig. 1. Schematic diagram of microwave absorber.

The X-ray diffraction patterns for the Ba₃Co_{2 (0.8-x)}Mn_{0.4}Ni_{2x}Fe₂₄O₄₁ samples were obtained at room temperature, using CuK_{α} radiation.

Mössbauer characterizations were performed in the transmission geometry, using a conventional spectrometer in a constant acceleration mode, with the gamma rays provided by a ⁵⁷Co(Rh) source. The Mössbauer spectra were analyzed with a non-linear least-square routine, with Lorentzian line shape.

The magnetization versus applied field measurements were taken on a ADE-HF-4 vibrating sample magnetometer (VSM), up to a maximum applied field of 20kOe.

TEM images and electron diffraction patterns were carried out on a JEOL 1230 transmission electron microscope at an accelerating voltage of 200 kV.

3. Results and discussions

3.1. Crystal structure

Figure 2 shows the X-ray diffraction patterns for the above-mentioned compositions. The diffraction patterns confirmed the presence of the Z-type hexaferrite phase structure in all samples. The variation of lattice parameters, *a* and *c*, their ratio $\frac{c}{a}$ and cell volumes (V) versus nickel substitution are given in Table 1. The lattice parameters were calculated from the relation:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{b^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$
(1)

where d_{hkl} is the interplanar distance.



 2θ (degrees)

Fig.2. XRD pattern of calcined powders at 1150 ° C. The result for the standard sample from JCPDS is shown at the bottom.

Table 1. The structural and magnetic parameters of Ba $_{3}$ Co $_{2}$ $_{(0.8-x)}$ Mn $_{0.4}$ Ni $_{2x}$ Fe $_{24}$ O $_{41}$.

Х	a(nm)	c(nm)	c/a	$V(nm)^3$	H_c (Oe)	M_s (emu/g)
0	0.5874	5.251	8.939	1.569	55	48
0.05	0.5876	5.257	8.946	1.571	53	42
0.1	0.5879	5.261	8.948	1.574	52	31
0.15	0.5883	5.266	8.951	1.578	48	27

The lattice parameters, *a* and *c*, increased from 0.5874 nm to 0.5883 nm and from 5.251 nm to 5.266 nm, respectively, as nickel substitution varied from 0 to 0.15. The unit cells expanded from 1.569 nm³ for Ba₃Co_{1.6}Mn_{0.4}Fe₂₄O₄₁ to 1.578 nm³ for Ba₃Co_{1.5}Mn_{0.4}Ni Fe₂₄O₄₁. The increase is attributed to the small cobalt ion radius of 0.065 nm, as compared to the nickel ion radius of 0.070 nm.

A TEM micrograph taken from the X=0.05 sample is shown in Figure 3.a. It is apparent that nanocrystalline particles were formed with a hexagonal shape of about 30 nm of grain size. Ultrafine particle sizes were approximately 70 nm. The electron diffraction pattern for the same selected area in the sample is shown in Figure 2.b. According to this figure, an increase in the number of points led to a ring form, which confirms the presence of nanosized particles.



Fig.3a.TEM micrograph of Ba $_{3}$ Co $_{1.5}$ Mn $_{0.4}$ Ni $_{0.1}$ Fe $_{24}$ O $_{41}$ calcined at 1150 \degree C for 2 h. b. Electron diffraction photograph of Ba $_{3}$ Co $_{1.5}$ Mn $_{0.4}$ Ni $_{0.1}$ Fe $_{24}$ O $_{41}$.

3.2 Magnetic properties

Figure 4 shows the magnetic hysteresis loops for the samples with different nickel content. The respective saturation manetizations, M_s , and coercive forces, H_c , are listed in Table 1. The M_s values were deduced from a numerical analysis (i.e., by using the linear least-sequare method) of the magnetization curves, based on the law of approach to saturation[14]:

$$M(H) = M_{s}(1 + \frac{A}{H} + \frac{B}{H^{2}} + ...) + \chi_{p}H,$$

where $H = H_0 - H_d$; H_0 is the applied field and H_d is the demagnetizing field of the samples. The coercive force was obtained directly from the cross-over points on the abcissa of the M - H loops.



Fig.4. Room temperature hysteresis loops of (a) x=0, (b) x=0.05, (c) x=0.1, (d) x=0.15.

The results show that all the samples exhibit typical soft magnetism and the substitution reduced the saturation magnetization and coercive force. It should be noted that saturation magnetization values are smaller than expected. This phenomenon can be attributed to the existing of a nonmagnetic layer existing on the surface of the nanoparticles [15]. It is well known that coercive force is heavily dependent upon grain size [16].

In Z-type ferrites, metallic ions such as Fe^{3+} , Co^{2+} , Mn^{2+} and Ni²⁺ are located in non-equivalent octahedral and tetrahedral sites. The Co^{2+} cation, specially, is a strongly magnetocrystalline anisotropic element and its partial replacement by Mn^{2+} or Ni²⁺ may lead to complex magnetic properties.

There are ten inequivalent crystallographic sites, designed by $12 k_{VI}$, $2d_V$, $4f_{VI}$, $4e_{VI}$,

 $4e_{IV}$, $4f_{IV}$, $4f_{VI}^*$, $4f_{VI}^*$, $12k_{VI}^*$ and $2a_{VI}$, according to the standard Wyckoff notation. Some crystallographic and magnetic properties of these ten sites are listed in Table 2 (taken from Ref. 13).

Site	Coordination	Block	Number of ions	Spin	Component
$12k_{VI}$	octahedral	R-S	6	up	
$2d_{V}$	fivefold	R	1	up	Ι
$4f_{VI}$	octahedral	R	2	down	
$4e_{VI}$	octahedral	Т	2	down	
$4e_{IV}$	tetrahedral	S	2	down	II + I V
$4f_{IV}$	tetrahedral	S	2	down	
$4f^*{}_{\scriptscriptstyle IV}$	tetrahedral	Т	2	down	
$4f^*_{VI}$	octahedral	S	2	up	
$12k^{*}_{VI}$	octahedral	T-S	6	up	III
$2a_{VI}$	octahedral	Т	1	up	

Table2.coordination, block location, the number of ions per formula unit, and spin direction in Z-type barium ferrite.

The Ni²⁺, Mn²⁺ and Co²⁺ ions have larger octahedral site preference than Fe³⁺ and, thus, Ni²⁺, Mn²⁺ and Co²⁺ occupy octahedral sites, where the spin direction is the same as the whole magnetic moment. Then, in our opinion, because Ni⁺² has a smaller magnetic moment than Co²⁺, the substitution of nickel for cobalt leads to the reduction of saturation magnetization.

3.3 Mössbauer analyzes

Figure 5 shows the room temperature Mössbauer spectra for the non-substituted and one representative substituted sample. All the spectra were fitted with, at least, six discrete sextets, corresponding to the ten metal sites of the hexaferrite structure[13]. In spite of being different crystallographic sites, some of them are magnetically similar and can not be separated in the fit procedure (see Table 2). The components were assigned according to Albanese and Li[13,17], although extra lines are present in our spectra. These may be attributed to the major diversity of atomic species in the iron neighborhood. An extra sextet, corresponding to residual metallic iron, was added (except for X = 0.15) in order to improve the fit quality. Eventually (i.e., for X = 0.05 and 0.10), a doublet belonging to the paramagnetic fraction of the sample was also included as an additional component. The subspectral areas were free to vary.



Fig.5. Mössbauer spectra for the X = 0 (a) and 0.15 (b) samples. — Ia — Ib — II — IIIa — IIIb — IV.

Table 3 presents the obtained hyperfine parameters and subspectral areas.

Figure 6 shows the average (i.e., by the subspectral areas) hyperfine magnetic field together with the saturation magnetization, as a function of X. It is observed that the average field, supposedly to reflect the sum of all iron magnetic moments is nearly constant, whereas the

saturation magnetization decreases with X. Definitely; this reveals no degradation of the iron magnetic lattice with increasing nickel content.



Fig.6. Variation of hyperfine magnetic field and saturation magnetization with X.

Table 3. Hyperfine parameters and subspectral areas for the Ba $_{3}$ Co $_{2}$ $_{(0.8-x)}$ Mn $_{0.4}$ Ni $_{2x}$ Fe $_{24}$ O $_{41}$ samples

Sample	Site	IS ^a (mm/s)	QS (mm/s)	$B_{\rm hf}$ (<i>T</i>)	Γ (mm/s)	Area (%)
X = 0	Ia	0.35	0.03	38.9	0.54	20.0
	Ib	0.33	0.28	41.0	0.36	18.2
	II	0.35	0.05	43.3	0.40	13.5
	IIIa	0.23	0.19	47.9	0.42	23.4
	IIIb	0.33	-0.05	46.4	0.35	11.3
	IV	0.37	0.12	50.8	0.30	12.2
	α-Fe	0.0	-	32.0	0.44	1.4
	Ia	0.35	0.02	38.9	0.55	21.4
	Ib	0.33	0.28	41.2	0.39	19.4
	II	0.37	0.04	43.7	0.49	12.2
V = 0.05	IIIa	0.28	0.10	48.8	0.36	16.8
$\mathbf{A} = 0.05$	IIIb	0.30	0.02	46.9	0.40	12.9
	IV	0.37	0.09	51.0	0.31	12.9
	Doublet	0.34	0.60	-	0.35	3.0
	α-Fe	0.0	-	32.7	0.23	1.4
	Ia	0.34	0.09	39.1	0.47	15.7
	Ib	0.34	0.23	41.4	0.39	22.3
	II	0.36	0.04	43.8	0.30	9.7
V = 0.10	IIIa	0.23	0.16	47.6	0.34	22.2
Λ - 0.10	IIIb	0.30	0.03	46.4	0.42	17.8
	IV	0.33	0.09	50.5	0.22	7.8
	Doublet	0.11	0.71	-	0.40	2.7
	α-Fe	0.0	-	33.0	0.40	1.8
X = 0.15	Ia	0.36	0.07	39.0	0.53	21.3
	Ib	0.34	0.29	41.1	0.31	16.0
	II	0.37	0.08	43.3	0.39	13.8
	IIIa	0.24	0.15	48.0	0.40	23.4
	IIIb	0.31	0.01	46.5	0.40	14.0
	IV	0.37	0.10	50.8	0.27	11.5

3.3. Absorption characteristics

The reflection loss is related to the normalized input impedance Z_{in} of a metal-backed microwave absorbing layer as [18]:

$$R(dB) = 20\log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|$$
(2)

with Z_{in} given by

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh[j\frac{2\pi}{c}\sqrt{\mu_r\varepsilon_r}fd], \qquad (3)$$

where μ_r and ε_r are the complex permeability and permittivity of the medium, c is the velocity of light in free space, f is the frequency and d is the absorber thickness.

The impedance matching condition is given by Z = 1, to represent the perfect absorbing properties. The 10 dB absorbing bandwidth means that the frequency bandwidth can achieve 90% of reflection loss, whereas a 20 dB absorbing bandwidth means that the frequency bandwidth can achieve 99% of reflection loss. The minimum absorber thickness and the frequency in the matching situation was defined as matching thickness (dm) and the matching frequency (fm), respectively.

Figure 7 shows the variation of the reflection loss versus frequency, observed in composite samples with 80%wt. of ferrites. It is well known that the natural ferromagnetic resonance absorption is dominative in the loss mechanism of the ferrite absorber materials, thus two matching frequencies are observed in all samples owing to the domain wall motion at lower frequency and spin resonance at higher frequency [19].



Fig.7. Absorption characteristics of the composite: (a) x=0, (b) x=0.05, (c) x=0.1, (d) x=0.15.

Table 4 lists the absorption data for the prepared hexaferrites. In the table, the bandwidth is defined as the frequency width in which the reflection loss is more than -15 dB. It

is evident that the doped hexaferrites have much more effective electromagnetic absorption effects.

Composition(x)	Minimum RL	d(mm)(RL<-	f(GHZ)	Frequency range
- · · /	Value(dB)	15dB)	(minimum RL)	(GHz) (RL
				<-15 dB)
0	20	2	19.7	0.5
0.05	40	2	18.6	3
0.1	35	2	16.4	5.5
0.15	27	2	14.4	0.6

Table 4. Electromagnetic wave absorption properties of composites with 80 wt% ferrites.

The reflection loss pattern for $Ba_3 Co_{1.6} Mn_{0.4} Fe_{24} O_{41}$ indicates that the minimum reflection loss with (-20dB) is at the frequency of 19.7 GHz (Fig.6a). Obviously, it appears that this concentration cannot be used as suitable wideband electromagnetic wave absorber at a thickness of 2 mm. The composition of $Ba_3 Co_{1.5} Mn_{0.4} Ni_{0.1} Fe_{24} O_{41}$ ferrite showed the highest microwave absorption. This is shown clearly in Fig.6b that the band which can be covered by this ferrite is about 3GHz with a reflection loss higher than -15 dB. The minimum reflection loss of this band is -40 dB at a matching frequency of 18.6 GHz.

For the Ba₃Co_{1.4}Mn_{0.4}Ni $_{0.2}$ Fe₂₄O₄₁ ferrite, the matching frequencies are equal to 16.4 and 18.2 GHz. In particular, a minimum reflection loss value of -35dB was observed at 16.4GHz (Fig.6c). The bandwidth covered by this ferrite is nearly 5.5 GHz, with reflection loss higher than -15 dB.

Figure 7.d shows the reflection loss curve for $Ba_3 Co_{1.3} Mn_{0.4} Ni_{0.3}$ Fe₂₄O₄₁ composition in frequency range from 12 to 20GHz. It can be seen that the bandwidth covered by this ferrite is more than 0.6GHz with reflection loss higher than - 15 dB. Minimum reflection loss is about -27 dB at a matching frequency of 14.4 GHz. This dispersion is due to the domain wall motion at lower frequency and spin resonance at higher frequency, respectively.

It should be noted that a good quality absorber should have a large reflection coefficient, a large bandwidth , and a small matching thickness. So, It is difficult to obtain all these characteristics in a single absorber.

According to Fig.7, if the bandwidth is defined as the frequency width in which the reflection loss is more than -15 dB, the composition of Ba₃Co_{1.4}Mn_{0.4}Ni_{0.2}Fe₂₄O₄₁ is the best one of them. Because, this material has wideband with value of about 5.5GHz. For the this reason, its value of reflection loss with different thicknesses was studied.

Figure 8 shows the variation of reflection loss versus frequency of the x=0.1 sample with 80% ferrite with different thicknesses. This shows a minimum RL = -38dB at f_m = 17.2GHz with the -15dB bandwidth over the extended frequency range of 16.4–18.8GHz for t_m =1.8 mm, a minimum RL = -35dBat f_m =16.4GHz with a -20dB bandwidth over the frequency range of 13.7–19.2GHz for t_m=2mm and -22 dB between 12.6 and 16.2GHz for t_m=2.2mm.

Fig.8 also shows that there is a minimum reflection loss of -40 dB at 12.5 GHz for thickness of 2.4 mm. Furthermore, it is evident that the position of minimum reflection loss peak is moving towards the lower frequency region with the increase of the absorber thickness.

It should be pointed out that the authors have reported that the M-type and W-type ferrites [19,20] can function as microwave absorbers in the gigahertz region. However, it is considered less the microwave absorption properties of Z-type barium ferrites in the 12-20 GHz frequency range. By comparing with other results achieved in previous studies [13,21], the prepared absorbing composites in this study have a higher reflection loss and better wideband ^{absorption} properties.



Fig.8. Absorption characteristics of Ba₃ Co_{1.4} $Mn_{0.4}$ Ni_{0.2} Fe₂₄ O₄₁:(a) t=1.8mm, (b) t=2mm, (c) t=2.2mm, (d) t=2.4mm

It is noteworthy that crystalline size plays a significant role in the microwave absorption properties . When the size is below a critical diameter, magnetic particles cannot support more than one domain. Magnetic structure varies from multiple domains to single domain. Studies [22,23] show that the surface spins of ferrite nanoparticles are disordered, and the exchange coupling between the surface and core gives rise to a variety of spin distributions within a single domain particle. The surface spin can result in a high hysteresis loss. Nanosized particles have a tremendous surface area and a high rate of atoms on surface, so the quantity of the dangling bond atoms is great. Moreover, with the reduction of particle size, the number of the atoms with unsaturated coordination on the surface is increased. These variations lead to the interface polarization and multiple scatter, which become one of the important factors to absorb microwave.The outlook of using nanocrystalline as microwave absorber is therefore quite promising.

4. Conclusions

The most important conclusions of our work can be summarized as follows:

(1) $\operatorname{Ba}_{3}\operatorname{Co}_{2}_{(0.8-x)}\operatorname{Mn}_{0.4}\operatorname{Ni}_{2x}\operatorname{Fe}_{24}\operatorname{O}_{41}$ hexaferrites were successfully prepared by the citrate sol-gel technique;

(2) All the Mn-Ni-substituted Co-Z ferrites exhibited typical soft magnetic character;

(3) Substitution of nickel for cobalt led to the reduction of saturation magnetization;

(4) Microwave absorbers for applications over 14 GHz, with satisfactory reflection losses, can be obtained at a thickness of 2 mm by controlling the manganese and nickel content in Co-Z hexaferrites.

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