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Effect of Co and Ni additions as doping materials on the micro-structures and the magnetic properties of barium hexa-ferrites

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ABSTRACT

In this paper, the synthesis of $BaFe_{12-2x}Co_xNi_xO_{19}$ (x = 0–0.2) materials at a calcination temperature of 950 °C using a co-precipitation method have been reported. The precursor concentrations of the mixture were varied to identify the optimum sample. The results suggested that the structure of barium hexa-ferrite crystal did not change due to the effect of Co and Ni additions. The optimum condition is obtained at the concentration of 0.2% mol of Co and Ni ions resulting a single phase of barium hexa-ferrite. The XRD analysis confirmed that the addition of Co and Ni affects the growth of barium hexa-ferrite crystals in plane (114). The optimum condition of the magnetic properties are listed in the following: $M_s = 34.83$ emu/g, $M_r = 18.03$ emu/g, $H_c = 2099$ Oe.

1. Introduction

Barium hexa-ferrite ($BaFe_{12}O_{19}$) have attracted more attentions due to its low cost, good chemical stability, high magnetic saturation and coercivity, excellent corrosion resistance and high curie temperature [1–4]. The magnetic properties of $BaFe_{12}O_{19}$ are affected by the substitution of Fe^{+3} and Ba^{+2} ions [5,6]. These substitution can be controlled using certain level of ion substitutions, such as; tetra-valence, di-valence of non and magnetic cations, ie: Mn, Mg, Al, Ni, Co, Cu and Zn [7–12]. Behera *et al* [13] reported that the effect of Ni addition in barium hexa-ferrite can decrease the magnetization saturation value with co-precipitation method.

Dawar *et al* [14] reported that nickel-doped barium nano hexa-ferrites ($BaNi_xFe_{(12\text{-}x)}O_{19}$) were prepared using the chemical co-precipitation technique, at calcination temperature of 800 °C for 4 h holding time. The use of nickel enhances the magnetization saturation and decreases the coercivity values. M-type barium hexa-ferrites $Ba_{1x}Co_xFe_{12}O_{19}$ (x = 0–0.25) with a doped material of Cobalt were synthesized by Chavan *et al* [9] using a sol– gel autocombination method. The materials were post-annealed at a relatively low temperature of 600 °C. The crystals are transformed from a pure barium-hexa-ferrite to a spinel with Co substitution. Another

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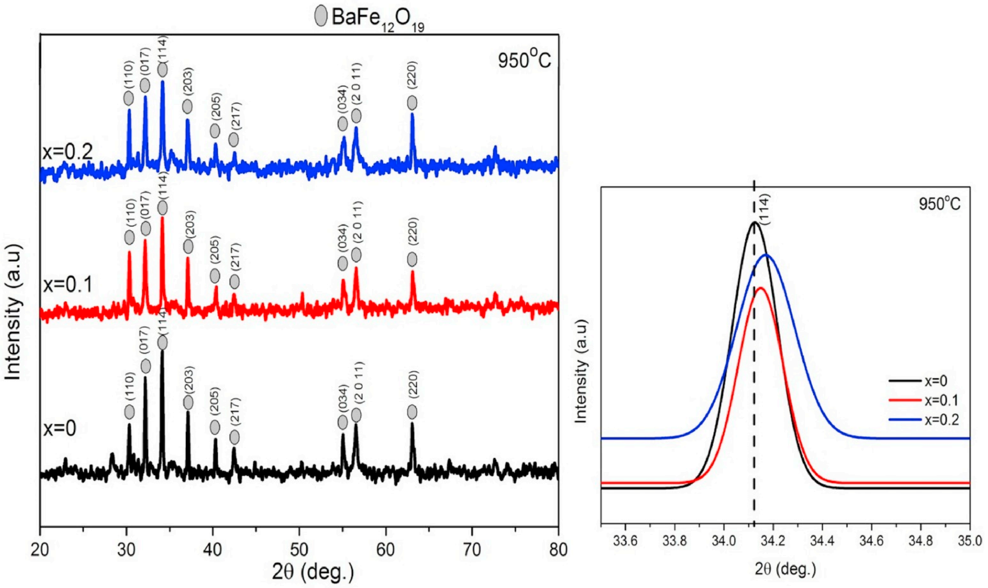


(a) (b)

Fig. 1. The XRD Patterns: (a) $BaFe_{12}O_{19}$ powder samples (x = 0–0.2) (b). Magnefication of the XRD patterns in fields (114).

Table 1
The parameters of the crystal samples of $BaFe_{12\text{-}2x}Co_xNi_xO_{19}$ (x = 0–0.2) in the crystal plane (114).

Sample	2θ (deg.)	*FWHM* (deg.)	*a* (Å)	*c* (Å)	*D* (nm)	ρ_{calc} (g/cm^3)
x = 0	34.13	0.25	5.88	23.23	33.41	5.31
x = 0.1	34.15	0.34	5.88	23.22	25.50	5.32
x = 0.2	34.17	0.28	5.89	23.24	29.73	5.35

research related to the use of Ni and Co as doped materials in barium hexa-ferrite were conducted by Giordani *et al* [8]. The authors synthesized the materials using the co-precipitation method by varying Ni and Co additions (x = 0–0.4) at a fixed calcination temperature of 1100 °C. The authors suggested that the material can be used as a magnetic loss material. Kanagesan *et al* [15] had substituted Ni and Co to Fe (x = 0–0.8) with calcination temperature 1150 °C for 3 h. The result suggested that the use of nickel and cobalt can be decreases the coercivity values.

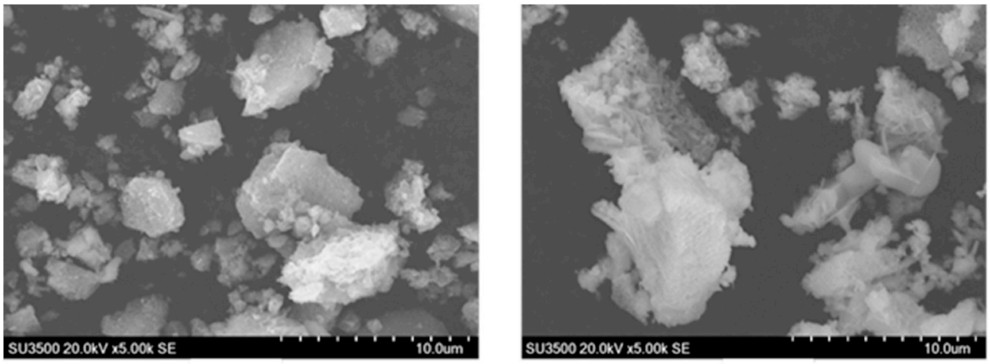
In this paper, the synthesis of barium hexa-ferrite by adding Co–Ni as doping materials using the co-precipitation were examined. The effect of the material concentrations doping in barium hexa-ferrite were varied to obtain an optimum condition to be used as a material candidate for micro-wave absorber application.

2. Materials and methods

Barium hexa-ferrite with doping materials of Ni and Co (x = 0–0.2)were synthesized using a co-precipitation method where barium chloride ($BaCl_2$), iron chloride ($FeCl_3$), cobalt chloride ($CoCl_2$), and nickel chloride ($NiCl_2$) were used as the raw materials. The materials were dissolved in 25 ml of HCl (37%) and magnetically stirred for 30 min at room temperature. Then, the iron sand solution was filtered using a filter paper of Whatmann (Grade 40 Circles). The solution was then mixed with aquadest of 50 ml in a beaker glass and was stirred using a magnetic stirrer at 500 rpm until homogeneous solution is obtained. The solution was washed 10 times using distilled water until a neutral pH of 7 is obtained and was dried in the oven for 15 h at a temperature of 100 °C. Then, the powder was calcinated at a temperature of 950 °C for 2 h and at a heating rate of 10 °C/min. The final powder of barium hexa-ferrite material were analyzed using X-ray Diffraction (Rigaku Smartlab), Vibrating Sample Magnetometer (VSM250 Dexing Magnet Ltd) and Scanning Electron Microscopy (JEOL).

3. Results and discussion

The XRD analysis of the samples at different addition of doping materials (x = 0–0.2) are shown in Fig. 1(a). The characterization confirmed that a single phase of $BaFe_{12}O_{19}$ occurred at the calcination temperature of 950 °C. Fig. 1(a) also present the change in the position of the diffraction peak and peak intensity as a result to the presence of Co and Ni in the hexagonal structure, causing changes in



(a) (b)

Fig. 2. SEM image of $BaFe_{12-2x}Co_xNi_xO_{19}$ (a) x = 0 (b) x = 0.2.

Table 2
EDS analysis of $BaFe_{12-2x}Co_xNi_xO_{19}$ (wt%).

Sample	Element content				
	Ba (wt%)	Fe (wt%)	Ni (wt%)	Co (wt%)	O (wt%)
x = 0	30.37	40.59	–	–	29.04
x = 0.2	17.24	60.47	0.76	1.12	20.41

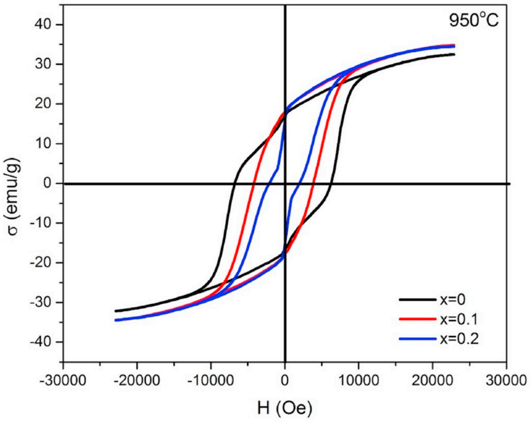


Fig. 3. Hysteresis curve of $BaFe_{12-2x}Co_xNi_xO_{19}$ powder (x = 0–0.2).

the lattice parameters of the compound [16]. This XRD analysis suggested that Co and Ni doping did not change the hexagonal structure of $BaFe_{12}O_{19}$ and a substitution process of Co and Ni to Fe is confirmed. The parameters of the crystal samples of $BaFe_{12-2x}Co_xNi_xO_{19}$ (x = 0–0.2) in the crystal plane (114) are given in Table 1.

Fig. 1(b) suggested that there is a peak shift of (114) towards a larger angle of 2θ as a result of the additions of Co and Ni. Thus, there is a decrease in the intensity values. This is occurs due to the addition of Co and Ni that affects the growth of barium hexa-ferrite crystals [17,18]. From Table 1, it can be observed that the lattice parameters of ‘a’ (5.88–5.89 Å) and ‘c’ (23.23–23.24 Å) are almost no different between sample without doping compared with the condition where the doping materials are existed. The substitution of Co and Ni ions in $BaFe_{12-2x}Co_xNi_xO_{19}$ occurs because of the radius difference of ion r(Co) = 0.72 Å, r(Ni) = 0.69 Å and r(Fe) = 0.63 Å [14,19]. In the current studies, the synthesized of $BaFe_{12-2x}Co_xNi_xO_{19}$ (x = 0–0.2) have a small crystallite size (<50 nm) and single phase that is suitable to be used as a potential candidate for microwave absorbing materials.

SEM-EDS results at different sample variations of x = 0 and x = 0.2 are presented in Fig. 2. The images suggested that the agglomeration occurred with random particle sizes of 4–6 μm. Sample x = 0 and x = 0.2, substituted Co and Ni ions increase (shown at Table 2) as comparable of the additions of Co and Ni. This condition is obtained due to the effect of the substitution of Co and Ni ions in $BaFe_{12-2x}Co_xNi_xO_{19}$ [11,20]. In Table 2 can also be seen that the content of Fe is the largest element in the sample. In the sample with x = 0.2, there were Co and Ni elements of 1.12 and 0.76 wt% respectively which showed that both elements were substituted into hexa-ferrite samples.

Table 3
Magnetic properties of $BaFe_{12-2x}Co_xNi_xO_{19}$ (x = 0–0.2).

Sample	Magnetic Properties		
	Saturation, Ms (emu g^{-1})	Remanence, Mr (emu g^{-1})	Coercivity, Hc (Oe)
x = 0	32.02	16.98	6958
x = 0.1	34.34	17.31	4233
x = 0.2	34.83	18.03	2099

The reason behind the trend line in Fig. 3 is due to the fact that Co and Ni ions have paramagnetic behaviors compared to Fe ion that has a ferromagnetic behaviour. The presence of Co and Ni ions makes the anisotropy of $BaFe_{12}O_{19}$ changed and decreasing the magnetic flux. The decrease in the magnetization saturation with the increase of Co and Ni concentrations is partly attributed to the smaller magnetic moment of Co and Ni as compared to Fe [21–23]. From Table 3 it can be seen that the good hexa-ferrite materials according to the requirement for microwave absorbent applications is the sample with low coercivity and high saturation. So, In this study, the sample with x = 0.2 is better candidates than other samples which fulfill these requirements.

4. Conclusions

The substitutions of Co and Ni ions as doping materials in $BaFe_{12-2x}Co_xNi_xO_{19}$ (x = 0, 0.1, and 0.2) using a co-precipitation method at a fixed calcination temperature of 950 °C are presented. The optimum condition of the sample is obtained at x = 0.2%mol concentrations of Co and Ni ions where a single phase of barium hexa-ferrite is occurred. The XRD analysis suggested that the addition of Co and Ni affect the growth of barium hexa-ferrite crystals. The VSM analysis confirmed that the addition of the doping materials (Co and Ni) decrease the magnetic properties to the range that is suitable for micro-wave absorber material.

CRediT authorship contribution statement

Masno Ginting: Conceptualization, Supervision, Writing - review & editing. **Perdamean Sebayang:** Conceptualization, Project administration, Validation, Writing - review & editing. **Martha Rianna:** Software, Writing - original draft. **Marhaposan Situmorang:** Visualization, Writing - review & editing. **Heryani Fujiati:** Methodology, Project administration. **Anggito P. Tetuko:** Data curation, Resources. **Eko Arief Setiadi:** Formal analysis. **Candra Kurniawan:** Funding acquisition. **Achmad Maulana Soehada Sebayang:** Investigation.

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