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Nanosize Effects on Magnetic Properties and Peak Shifting of X-Ray Diffraction Pattern of $BaFe_{12}O_{19}$ Produced by Sol Gel Method

Dwita Suastiyanti[a], Bambang Soegijono[b], M.Hikam[c]

[a]Graduate Program of Material Science, Department of Physics
University of Indonesia, Depok 16424, Indonesia

[a]Mechanical Department of Indonesia Institute of Technology (ITI)
Puspiptek-Serpong, Indonesia

[b,c]Multiferroic Laboratory, Department of Physics
University of Indonesia, Depok 16424, Indonesia

[a]dwita_suastiyanti@yahoo.com, [b]bambangsg11@yahoo.com,[c]m.hikam@gmail.com

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Abstract. The formation of barium hexaferrite, $BaFe_{12}O_{19}$ single phase with nanosize crystalline is very important to get the best performance especially magnetic properties. The samples were prepared by sol gel method in citric acid-metal nitrates system. Hence the mole ratios of Ba^{2+}/Fe^{3+} were varied at 1:12 and 1:11.5 with pH of 7 in all cases using ammonia solution. The solution was then heated at 80-90^{o}C for 3 to 4 hours. Then it was kept on a pre- heated oven at 150^{o}C. The samples were then heat treated at 450^{o}C for 24 hours. Sintering process was done at 850^{o}C and 1000^{o}C for 10 hours.Crystallite size was calculated by X-Ray Diffraction (XRD) peaks using scherrer formula. To confirm the formation of a single phase, XRD analyses were done by comparing the sample patterns with standard pattern. The peak shifting of pattern could be seen from XRD pattern using rocking curves at extreme certain 2θ. It was used MPS Magnet – Physik EP3 – Permagraph L to know magnetic characteristics. This method can produce $BaFe_{12}O_{19}$ nanosize powder, 22-34 nm for crystallite size and 55.59-78.58 nm for particle size. A little diference in nanosize affects the peak shifting of XRD pattern significantly but shows a little difference in magnetic properties especially for samples at 850^{o}C and 1000^{o}C with mole ratio of 1:12 respectively. The well crystalline powder is formed at mole ratio of 1:11.5 at 850^{o}C since it has the finest particle (55.59 nm) and crystalline (21 nm), the highest remanent magnetization (0.161 T) and the lowest intrinsic coersive (275.8 kA/m). It is also fitting exactly to the standard diffraction pattern with the highest value of best Figure of Merit (FoM), 90%. XRD peak position of this sample is almost same with XRD peak position of another sample with sinter temperature 1000^{o}C at same mole ratio.

Introduction

Nanostructured magnetic materials have been intensively investigated due to their applications in magnetic recording media, sensors and biomolecular separations [1]. Fine particles are one of the most commonly used materials in magnetic recording applications and have ability to absorb electromagnetic radiation in microwave range. Barium hexaferrite, $BaFe_{12}O_{19}$ (BHF) has been widely used in permanent magnetic materials, owing to excellent chemical stability and corrosion resistivity. Also along with further research and increasing demands for microwave communication, microwave dark room, the anti-electromagnetic wave radiation, raw material of multiferroic, the BHF has been caused great attention [2]. The arrangement of the 12 Fe^{3+} ions in the unit cell is as follows; two ions in the tetrahedral sites (four nearest O^{2-} neighbors), nine ions in the octahedral sites (six nearest O^{2-} neighbors) and one ion in the hexagonal site (five nearest O^{2-} neighbors). Materials of this type have a strong uniaxial magnetic direction, making as permanent magnets [3].

The magnetic properties arise from interactions between metallic ions occupying particular positions relative to the oxygen ion in its hexagonal crystalline structrue [4]. For a better performance, coupling between the magnetic grains should be decreased which can be achieved by

synthesizing finer single-domain particles with narrow size distribution. In other words, magnetic properties of this material depend mostly on its microstructure and particle size which are very much affected by preparation conditions [5].

So far various techniques have been proposed for the synthesis of BHF and these mainly include the conventional ceramic process of solid-state reaction, co-precipitation/hydrothermal synthesis, sol gel process, spray pyrolysis, molten salt method, etc. In these methods procedure, the formation of BHF all undergoes the intermediate phase. Whereas the intermediate phase transformation is often overlooked in the formation of BHF process [6]. In fact, the different intermediate phase transformation will have a great impact on the magnetic properties of BHF. Particularly, sol gel technique is a new method which can be used to prepare nanocrystalline BHF [7]. In solid-state reaction method, BHF particles could only be synthesized after long (20 hours) and high temperatures sintering (>1200^{o}C) which causes growing of grains in an uncontrollable manner [8].

Recently, this work could succeed to synthesize single phase BHF with citric acid-metal nitrates system after sintering at much lower temperatures (850^{o}C) for a shorter period of time, 10 hours. It is aimed at investigating the detail process of synthesis single BHF powder based on the effects of the different parameters leading to variable of crystallite and particle size. Also the relationship between the nanosize of BHF and peak shifting of X-Ray Diffraction (XRD) pattern that could affecting formation of BHF in single phase and magnetic properties.

Experimental Procedure

The nanosize BHF are synthesized by using sol gel technique. The starting materials were iron nitrate $Fe(NO_3)_3.9H_2O$, barium nitrate $Ba(NO_3)_2$, citric acid $C_6H_7O_8$ and ammonia solution NH_4OH, all of analytic purity (99.0%) from Merck KGaA Chemicals, Damstadt, Germany. An appropriate amount of $Fe(NO_3)_3.9H_2O$ and $Ba(NO_3)_2$ in molar ratios of Ba^{2+}/Fe^{3+} of 1:12 and 1:11.5 were dissolved in a minimum amount of deionized water to get a clear solution. Citric acid was added into the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+}, stirring for a few minutes until turning into the solution. Then ammonia solution was added to adjust the pH of 7 until the mixed solution getting into brown. The solution was evaporated to dryness by heating at 80-90^{o}C on a hot plate with continous stirring. As the water evaporated, the solution became viscous and finally formed a very viscous brown gel then kept it in oven at 150^{o}C for 5 hours. Most of the moisture in the viscous brown gel was evaporated and formed dried gel after heating at 450^{o}C for 24 hours. Afer grinding in the mortar, the dried gel was sintered at 850^{o}C and 1000^{o}C for 10 hours respectively.

The powder was identified by XRD Phillips, PW 1835 Type in the 20^{o}-100^{o} using CuKα radiation. It could be drawn some rocking curves at extreme certain 2θ from XRD pattern results. It could be known peak shifting of XRD pattern from these curves relating to nanosize of BHF powder.The crystallite size was calculated using Scherrer's relationship : $D = (k\lambda) / (B\cos\theta)$ where D is the average diameter in nm, k is the shape factor, B is the broadening of the diffraction line measured half of its maximum intensity in radians, λ is the wave length of x-ray and θ is the Bragg's diffraction angle. Particle Size Analyzer (PSA) of Malvern "Zeta Nanosizer" type was used to know particle size of BHF powder. It was used MPS Magnet – Physik EP3 – Permagraph L to know the magnetic characteristics.

Results and Discussion

The effects of mole ratios of Ba^{2+}/Fe^{3+} = 1:12 ; 1:11.5 and sinter temperatures 850^{o}C and 1000^{o}C on the XRD pattern can be shown in Fig 1. It confirms that all samples are in a single phase.

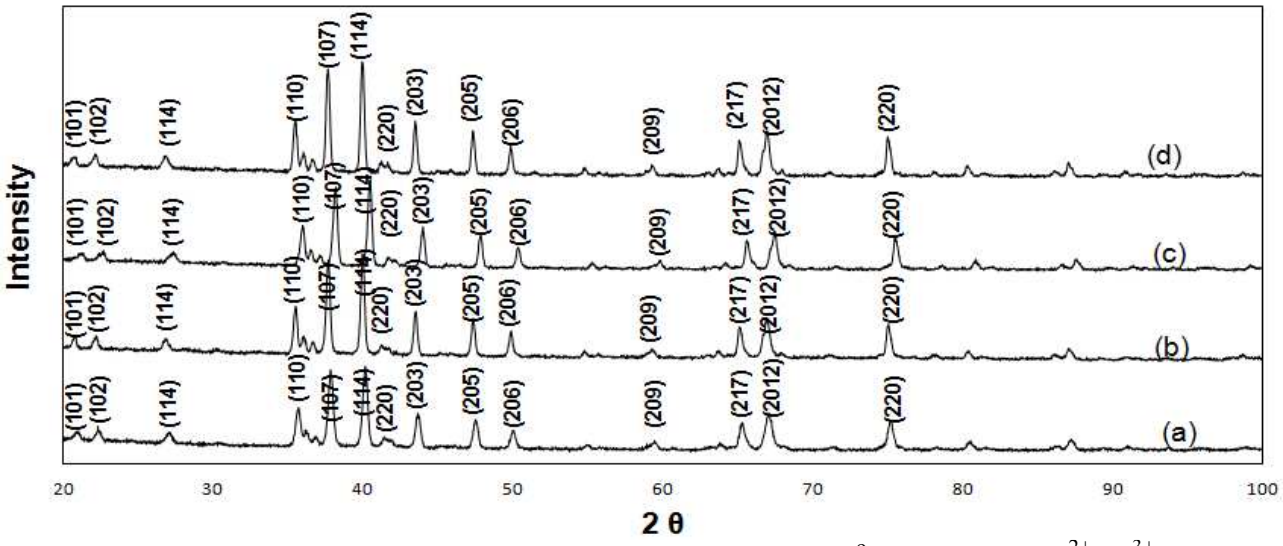


Figure.1. X-Ray Diffraction Pattern of Samples : (a) Sinter at 850°C 10 Hours (Ba^{2+}/Fe^{3+} = 1:12), (b) Sinter at 850°C 10 Hours (Ba^{2+}/Fe^{3+}=1:11.5),(c) Sinter at 1000°C 10 Hours (Ba^{2+}/Fe^{3+}=1:12), (d) Sinter at 1000°C 10 Hours (Ba^{2+}/Fe^{3+}=1:11.5)

Fig.1 shows that there are no traces of impurities phases $BaFe_2O_4$ and αFe_2O_3 which may contribute to the reduction of magnetic properties. All samples match with the standard powder diffraction file no.99-100-9621 from PDF2-PCPDFWin database. It could be converted to the value of best Figure of Merit (FoM) indicates the matching of sample pattern to the standard diffraction pattern shown in Table.1.

Table.1.Fitting of The Diffraction Patterns Based on The Standard Database

No	Mole Ratio Ba^{2+}/Fe^{3+}	Sinter Temperature	Standard Diffraction Pattern	Best FoM
1	1:12	850°C 10 Hours	$BaFe_{12}O_{19}$	88%
2	1:12	1000°C 10 Hours	$BaFe_{12}O_{19}$	79%
3	1:11.5	850°C 10 Hours	$BaFe_{12}O_{19}$	90%
4	1:11.5	1000°C 10 Hours	$BaFe_{12}O_{19}$	90%

From Table 1, it could be seen that samples with sinter temperatures 850°C and 1000°C for 10 hours and mole ratio of 1:11.5 almost match exactly with the standard powder since they have the highest value of best FoM 90%. It also could be known that there is a little peak shifting of XRD pattern among all ratios based on the difference of 2 θ and intensity value. The peak shifting could be shown clearly from rocking curves at certain 2 θ taken from Fig. 1 for all samples shown in Fig. 2,3,4 and 5.

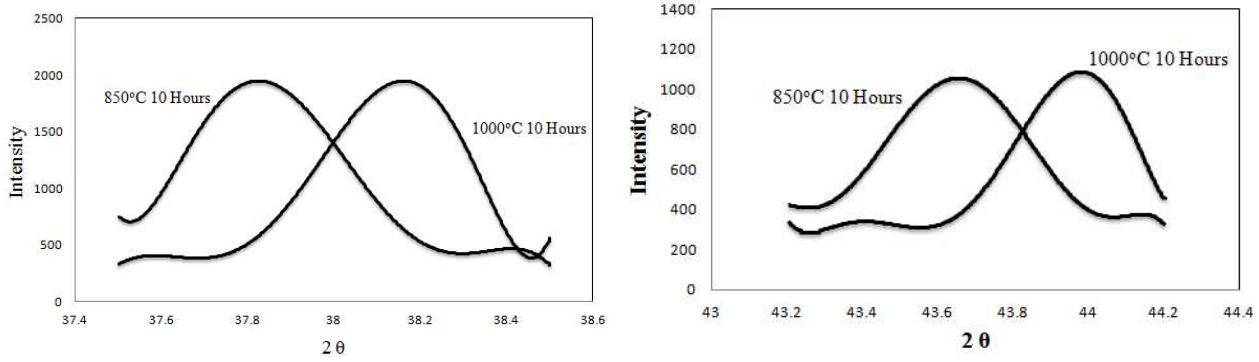
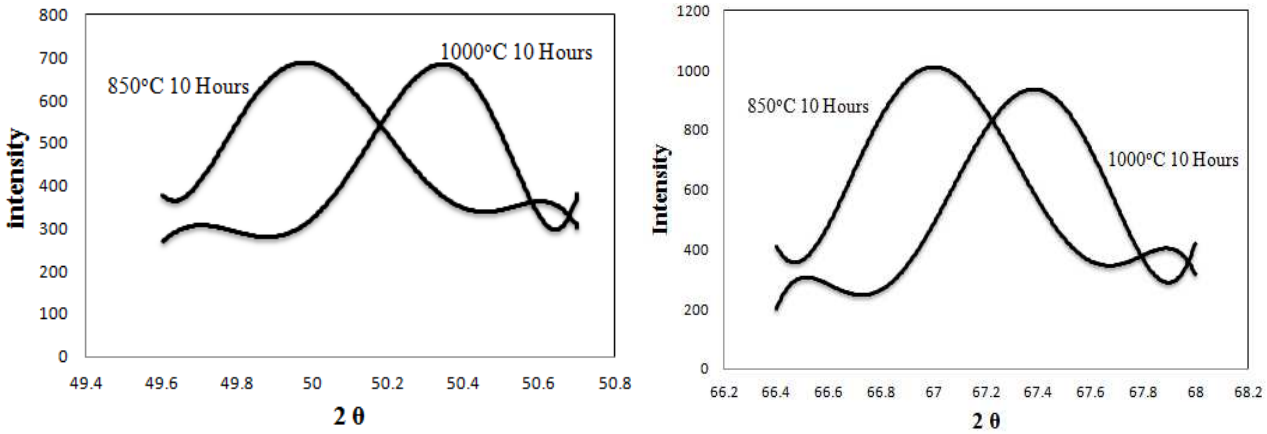
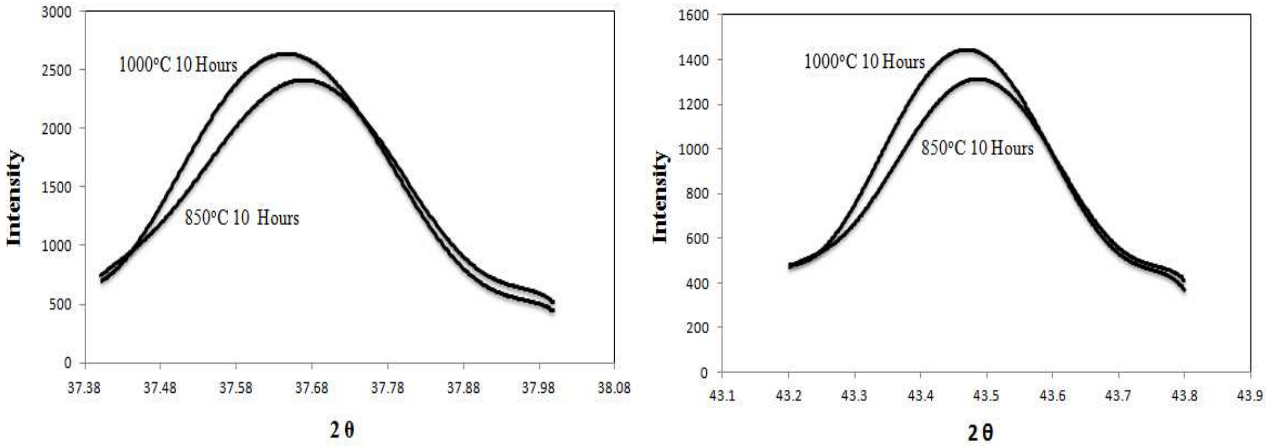


Figure.2.Rocking Curves for Peak Shifting of XRD Pattern of Samples with Mole Ratio of 1:12 at 37.4°-38.6°(a) and 43.2°-44.2° (b)



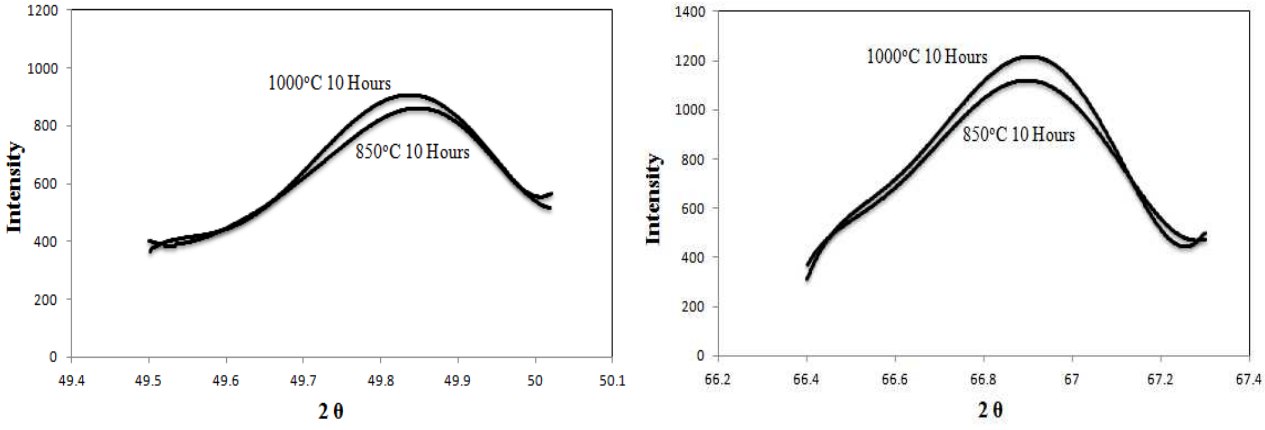
(a) (b)

Figure.3.Rocking Curves for Peak Shifting of XRD Pattern of Samples with Mole Ratio of 1:12 at 49.6°-50.8°(a) and 66.4°-68° (b)



(a) (b)

Figure.4.Rocking Curves for Peak Shifting of XRD Pattern of Samples with Mole Ratio of 1:11.5 at 37.38°-37.98°(a) and 43.2°-43.8°(b)

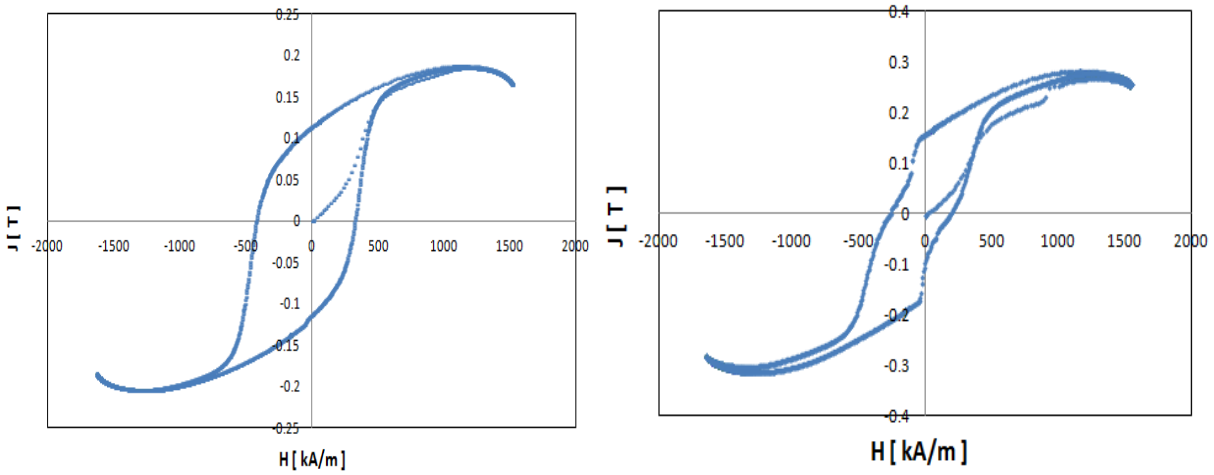


(a) (b)

Figure.5.Rocking Curves for Peak Shifting of XRD Pattern of Samples with Mole Ratio of 1:11.5 at 49.5°-50°(a) and 66.6°-67.2°(b)

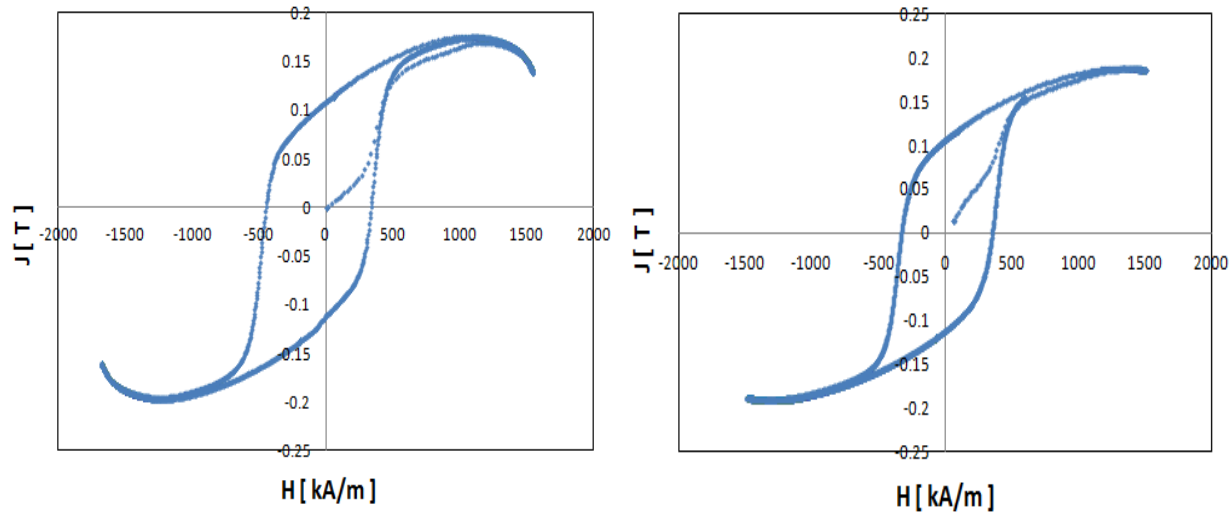
From Fig. 2,3,4 and 5, it could be known that peak shifting of XRD pattern for samples of mole ratio of 1:12 at 850°C and 1000°C is more wider than of mole ratio of 1:11.5 at same temperatures. There are differences in intensity values for mole ratio of 1:11.5 at 850°C and 1000°C, more enough than of mol ratio of 1:12 at same temperatures.The intensity value of mole ratio of 1:11.5 at 1000°C is higher than at 850°C.

Magnetic characteristic of samples could be seen in Fig.6 and 7 as a hysteresis loop curves.



(a) (b)

Figure.6 Hysteresis Loops of (a) Sample at Sinter 850°C for Mole Ratio of Ba^{2+}/Fe^{3+} = 1:12 and (b) Sample at Sinter 850°C for Mole Ratio of Ba^{2+}/Fe^{3+} = 1:11.5



(a) (b)

Figure.7 Hysteresis Loops of (a) Sample at Sinter 1000°C for Mole Ratio of Ba^{2+}/Fe^{3+} = 1:12 and (b) Sample at Sinter 1000°C for Mole Ratio of Ba^{2+}/Fe^{3+} = 1:11.5

Magnetic behaviors of as-synthesized BHF presented in Fig. 6 and 7 show that all of the samples are hard magnetic. Remanent magnetization value of sample at sinter temperature 850°C is higher compared to the sample at 1000°C for mole ratios of 1:12 and 1:11.5 but decreasing sinter temperature could reduce value of intrinsic coersive. As a matter of fact the characteristic differences in peak shifting of XRD pattern due to differences in nano size have a relation with magnetic properties of samples shown in Table 2.

Table.2. Crystallite, Particle Size and Magnetic Properties of All Samples

Mole Ratio Ba^{2+}/Fe^{3+}	Sinter Temperature (°C)	Remanent Magnetization (T)	Intrinsic Coersive (kA/m)	Crystallite Size (nm)	Particle Size (nm)
1:12	850°C 10 Hours	0.115	427.3	32	74.44
1:12	1000°C 10 Hours	0.110	453.2	34	78.58
1:11.5	850°C 10 Hours	0.161	275.8	22	55.59
1:11.5	1000°C 10 Hours	0.108	336.4	29	69.47

Table 2 shows that the differences in crystallite and particle size for samples at mole ratio of 1:12 at 850^{o}C and 1000^{o}C are little, but more enough than of mole ratio of 1:11.5 at same temperatures. It also happens to magnetic properties that there are little differences in magnetic properties (remanent magnetization and intrinsic coersive) for samples at mole ratio of 1:12 at same temperatures. At each mole ratios of 1:12 and 1:11.5, there is an increasing crystallite and particle size with increasing sinter temperatures due to growing grains at higher temperature.

Summary

It can be concluded that $BaFe_{12}O_{19}$ powder with nanosize (<100 nm) can be produced using the sol gel method. Sinter temperatures and mole ratios of Ba^{2+}/Fe^{3+} have an important influence on peak shifting of diffraction pattern, nanosize of crystallite and particle of powder and magnetic properties. It is also a relation between nanosize and peak shifting of XRD pattern affecting magnetic properties of samples. A little diference in nanosize affects the peak shifting of XRD pattern significantly shown for samples at 850^{o}C and 1000^{o}C with mole ratio of 1:12 respectively. Little differences in nanosize also show little differences in magnetic properties shown for sample with ratio of 1:12 at 850^{o}C and 1000^{o}C but peak shifting of XRD pattern at these parameters are wide enough. Much differences in nanosize also show much differences in magnetic properties shown for sample with ratio of 1:11.5 at 850^{o}C and 1000^{o}C but it has almost same position of XRD peak at these parameters. The well crystalline powder is formed at mole ratio of 1:11.5 at 850^{o}C since it has the finest particle and crystalline, the highest remanent magnetization, the lowest intrinsic coersive and shows XRD peak position which is almost same with XRD peak position at another sinter temperature of 1000^{o}C at same mole ratio.

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