

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF NANO-PARTICLES BSCNGCO SUPERCONDUCTORS AT ROOM - TEMPERATURE

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ABSTRACT: Synthesis of nano-particles $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ (BSCNGCO) superconductors has been successfully done by the wet mixing method. The aim of the study was to produce nanoparticles of BSCNGCO superconductors and study magnetic properties at room temperature. In this research, the raw material used in the formation of BSCNGCO superconductors is Bi_2O_3 (99.9%), SrCO_3 (99.9%), CaCO_3 (99.9%), CuO (99.9%), Nd_2O_3 (99.9%) and Gd_2O_3 (99.9%). The synthesis process was conducted by added with HNO_3 and mixing by a magnetic stirrer to obtain a homogeneous solution, then continued with the calcination process at 450°C for 2 hours and 600°C for 1 hour. The sintering process is done at 830°C with a variation of time, that is 10, 20 and 30 minutes. The result of XRD characterization is dominated by BSCNGCO with 2223 phases and BSCNGCO with 2212 phases, but there are still impurities in each sample such as Bi_2CuO_4 and $\text{Bi}_2\text{O}_{2.7}$. The addition of sintering time in 10, 20 and 30 minutes resulted in the addition of fractional volume values of BSCNGCO with 2223 phases, respectively 42.39%, 47.85%, and 49.42%. In contrast, the fraction of the phase volume of impurities (Bi_2CuO_4 , BSCNGCO with 2212 phases, $\text{Bi}_2\text{O}_{2.7}$) decreases with the addition of sintering time. From the results of TEM morphology and calculations using the Scherrer equation, we can determine the particle size of sample superconductors. The addition of sintering time in 10, 20 and 30 minutes resulted in increased particle size, respectively 25.61 nm, 26.10 nm and 30.08 based on calculations using the Sherrer equation. While the calculations using the ImageJ program of the TEM results of 0.2 nm and 0.5 nm, for the sintering time of 10 and 20 minutes respectively. The results of the VSM characterization of the sample exhibit ferromagnetic properties at room temperature. The addition of sintering time causes the saturation magnetization (M_s), a remanent magnetization (M_r) and coercive force (H_c) values to decrease. Samples of superconductors with sintering time of 10 and 20 minutes showed M_s values of 0.155 emu/g and 0.157 emu/g, M_r values of 0.012 emu/g and 0.011 emu/g, H_c values of 528.623 Oe and 473.327 Oe, respectively.

Keywords: wet-mixing, superconductor, XRD, TEM, VSM, nanoparticles, ferromagnetic

1. INTRODUCTION

The BSCCO superconductors have three phases, namely Bi-2201, Bi-2212 and Bi 2223. Of the three phases, the most potent to apply is Bi-2223, because it has the highest critical temperature (110 K). Assessment of experimental aspects and application of superconductors has been done by many researchers. The Bi-2223 phases still cannot be made in the form of single crystals, hence until now, researchers are still done to obtain its single crystal or to increase the critical current density and increase the critical magnetic field at high temperature.

Along with the current of globalization, technological progress is growing rapidly. One of the innovations made is nanotechnology. The basic principle of nanotechnology is the size of particles ranging from 1 to 100 nm [1], very small devices can provide performance results that cannot be obtained when using bulk materials. The

interesting thing about developing nanotechnology is because the material properties that include physical, chemical and biological properties change as the material dimension enters the nanometer scale.

Nano-particle research has been widely used, both for superconductor materials and other materials, such as by Shipra, et.al [2, 3]. In this study showed that oxide nano-particles exhibit ferromagnetic properties in accordance with predictions. This observation corresponds to the prediction that all oxide nanoparticles are on the surface of the particles. This ferromagnetic origin is due to the emergence of the magnetic moment of the oxygen vacuum on the particle surface. While in the sample with bulk particle size, YBCO at room temperature showed paramagnetic behavior. These results strengthen the ferromagnetic on the surface of oxide nanoparticles. This results in the presence of ferromagnetic persistence in nano-particle superconductors. For this purpose

measured $M(H)$ transition at 91 K temperature, ferromagnetic hysteresis still exists with increasing sufficiency of 300 Oe. In reality, it is difficult to keep ferromagnetic under the critical temperature of the magnetic measurement.

Particularly about the substitution of rare earth elements in BSCCO superconductors, some researchers have done so. Rentschler et.al, in 1992 had tried to replace Ca with Nd. From this research, it is known that the replacement of Ca with Nd can replace the position of Ca in crystal structure well and can give a good enough effect to increase the critical current density (J_c) [4].

Gd-related doping studies on the Bi-2223 phase superconductor were also performed by H. Aydin, et al., in 2009 [5]. Based on these studies it is known that Gd doping in the forming $\text{Bi}_{1.8}\text{Pb}_{0.35}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_3\text{Gd}_x\text{O}_y$ superconductors can decrease critical temperature T_c phase Bi-2223. Also, substitution of RE (rare earth) elements to BSCCO superconductors has been done, such as of Nd, Gd and Eu elements for the BSCCO-2212 superconductors.

Research related to that substitution has been done by Suharta, et.al [6]. RE substitution is not only used in BSCCO superconductors alone, but some researchers also use to replace the Y element on the YBCO superconductors. One of them is Suharta, et.al, who have synthesized REBCO superconductors by using wet mixing method and sintering temperature variation [7].

In this study, synthesis of BSCCO superconductors has been done with the substitution of rare earth elements (RE) on the element of Ca. This study focused on the formation of the crystal nanoparticles of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors, at the variation of sintering time to know the nanoparticle growth of Bi-2223 phase doped with Nd and Gd. The use of Nd and Gd doping is done to improve the critical magnetic field because it is known that elements of Nd and Gd are rare earth elements that are magnetic. The aim of this study is to know the influence of sintering time variation of particle size of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors. Besides that, how does sintering time variation effect on the lattice parameter and how is the magnetism of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors.

To see the success of this research, the samples were characterized using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Vibrating Sample Magnetometer (VSM).

Once characterized proceed with data analysis using software such as Match! 3.4.2 Build 96 [8], Rietica [9] and Image-J.

2. EXPERIMENT

In this study used the Bi_2O_3 (99.9%), SrCO_3 (99.9%), CaCO_3 (99.9%), CuO (99.9%), Nd_2O_3 (99.9%) and Gd_2O_3 (99.9%) raw materials. The synthesis process follows: the first is weighing, where each of the initial compounds according to the molar compounds. The second, each compound was added with HNO_3 and then stirred using a magnetic stirrer for 3 days until a homogeneous solution was obtained. The third, the homogeneous solution is heated at below 100°C to crust. The fourth, crust compound was calcinated at 450°C for 2 hours and continued at 600°C for 1 hour. The five, sintered at 830°C with a variation of sintering time, which is 10, 20 and 30 minutes.

The success of the synthesis of BSCNGCO superconductors of nano-particles can be seen by characterizing the Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Vibrating Sample Magnetometer (VSM), which is then analyzed using Match, Rietica, and Image-J. The flow diagram of the synthesis process is shown in the Fig. 1.

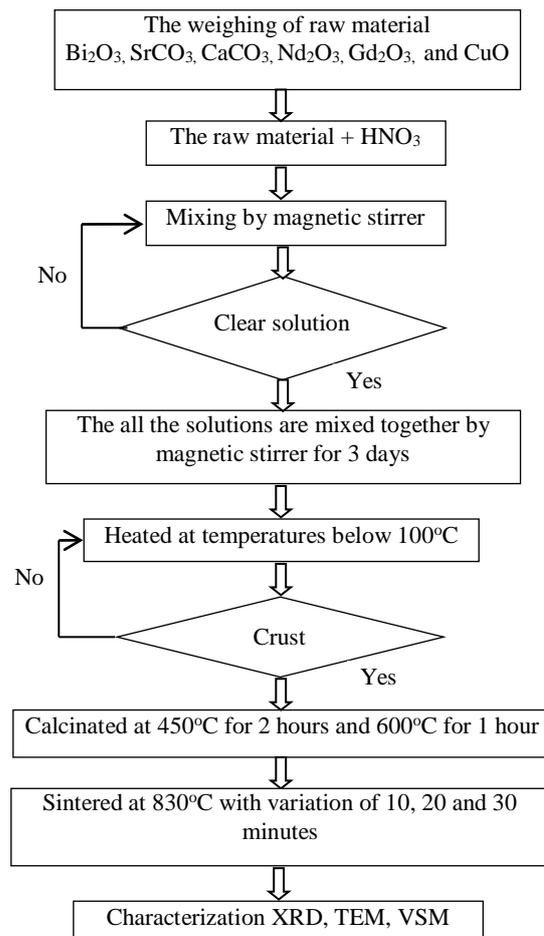


Fig.1 The synthesis process of BSCNGCO superconductor

3. RESULTS AND DISCUSSIONS

The XRD characterization is performed at an angle between 5-90°. The XRD characterized the diffraction pattern of the four BSCNGCO superconductor samples were calcined gradually at 450°C for 2 hours and 600°C for 1 hour and sintered at 830°C with three different time variations ie 10, 20 and 30 minutes can be seen in Fig. 2. In general, it can be seen that the result of XRD characterization gives rise to sharp peaks indicating that crystallization has occurred as well. Samples that have been calcinated at 600°C and sintered at 850°C for 10, 20 and 30 minutes are each marked BSCNGCO (10), BSCNGCO (20) and BSCNGCO (30). While the samples through the calcination process 600°C only are given symbols BSCNGCO (cal).

From the figure, it can be seen that the $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ samples through the sintering process with the temperature at 830°C for 10, 20 and 30 minutes have almost the same diffraction pattern. In contrast, compounds that only go through the calcination process at 600°C have a very different pattern. The spectrum is dominated by the occurrence of the BSCNGCO with 2223 and 2212 phases with high intensity and the appearance of the phase of impurities with small intensity. The difference between the result indicated that the crystal former of the $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors began to occur at 830°C, whereas at 600°C there was a small crystal formation of the $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$.

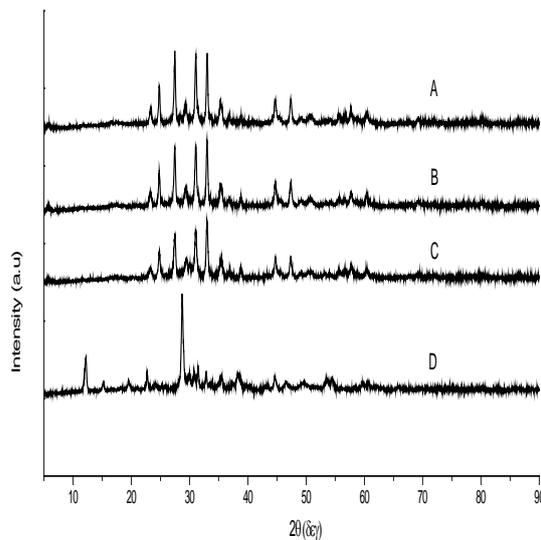


Fig.2 XRD pattern of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors : A: BSCNGO (30), B: (BSCNGO (20), C: BSCNGO (10), D: BSCNGO (Cal)

The phase identification is done by using the Match program. From the analysis result, it is known that there are still different impurities and phases in each sample as shown in Fig. 3. In the figure, the circle symbol is BSCNGCO-2223, the square symbol is the impurity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, the diamond symbol is the impurity of $\text{Bi}_2\text{O}_{2.7}$, and the triangle symbol is the impurity of Bi_2CuO_4 . Based on Fig. 3 it can be seen that at 830°C with a sintering time of 10, 20 and 30 minutes indicating the $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductor has not been formed perfectly yet, it is still characterized by the existence of impurities on the sample. Therefore, it takes longer sintering time to produce a compound without impurities. The matching results at angles of 22 to 40° are shown in Fig. 3.

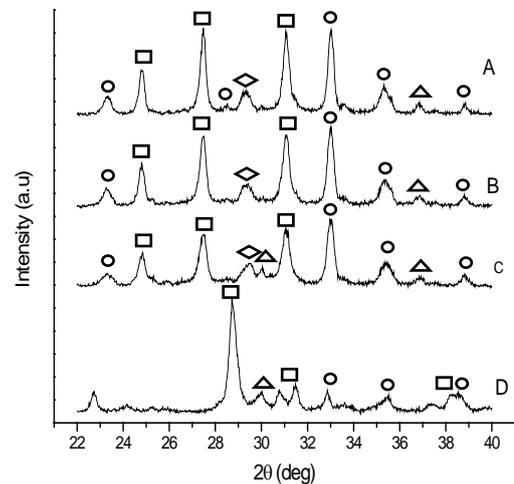


Fig.3 XRD pattern of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductor at 22-40°. A: BSCNGO (30), B: (BSCNGO (20), C: BSCNGO (10), D: BSCNGO (Cal)

Based on the analysis using Match! 3.4.2 Build 96 can be seen as the percentage of the formation of superconductor and impurity phases through the calculation of volume fraction (FV) in each sample. From the data of table 1 showed that the addition of sintering time resulted in the increased BSCCO superconducting volume fraction, while the volume fraction of the impurities decreased.

Rietveld analysis of characterization of XRD spectrum pattern analyzed using Rietica program, to know the value of lattice parameter each sample. The result of lattice parameter analysis of all samples is shown in Table 2. The addition of sintering time results in the value of the lattice parameter toward the a, b and c-axes decreases. This indicates that there are light atoms emitted from the bonds of atoms and molecules, especially

those atoms occupying the empty space in the unit cell. the addition of the lattice parameter values also causes the volume of the unit cell to increase, while the unit cell density decreases.

Table 1 The value of volume fraction of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors (BSCNGCO), and Bi_2CuO_4 (BCO), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (BSCCO), $\text{Bi}_2\text{O}_{2.7}$ (BO) impurities

Sample	Volume Fraction (%)			
	BSCNGCO	BCO	BSCCO	BO
BSCNGCO (Cal)	10.41	8.43	73.23	7.93
BSCNGCO (10)	42.39	5.68	46.14	5.79
BSCNGCO (20)	47.85	2.95	45.29	3.91
BSCNGCO (30)	49.42	1.80	45.21	3.57

Table 2. The value of lattice parameters of BSCNGCO

Sample	Lattice parameters		
	a (Å)	b (Å)	c (Å)
BSCNGCO (Cal)	4.05331	4.05331	39.55115
BSCNGCO (10)	3.84336	3.84336	38.89915
BSCNGCO (20)	3.83463	3.83463	38.89167
BSCNGCO (30)	3.83411	3.83411	38.85706

The particle size of each sample can be known by performing calculations using the Scherrer equation. The result obtained after characterization using TEM is an image showing the size of the crystals formed. The results are then analyzed using ImageJ software (Wayne Rasband) and OriginPro. Characterization by using TEM aims to determine the surface morphology of the $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors which cannot be seen using ordinary microscopy. The result of the characterization of TEM as shown in Fig. 4 and 5, then analyzed by using Image J and OriginPro 2016 software (Fig. 6 and 7). Based on data

analysis that has been done, it is known that this research has succeeded to form the crystal of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors in nanometer size. The average crystal size was obtained for the sample that calcined at 450°C for 2 hours and 600°C for 1 hour and superconductor that sintered at 830°C in 10 minutes. The effect of sintering time on the particle size of $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors is an agglomeration of crystal size so that increasing sintering time causes the increase of particle size. There is a difference of value between particle size with Scherrer and image calculations. This is understandable since the Scherrer calculations cover the entire spectrum that appears in the sample, whereas the calculations with images, cover only a small part of the surface state of the sample.

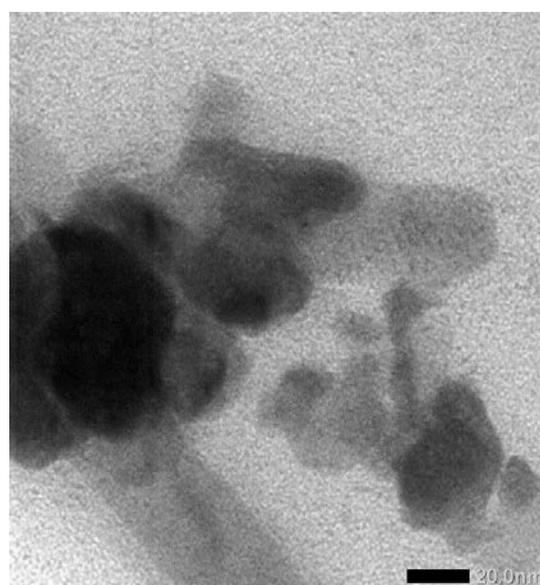


Fig.4 SEM images of the sample that calcined at 450°C for 2 hours and 600°C for 1 hour

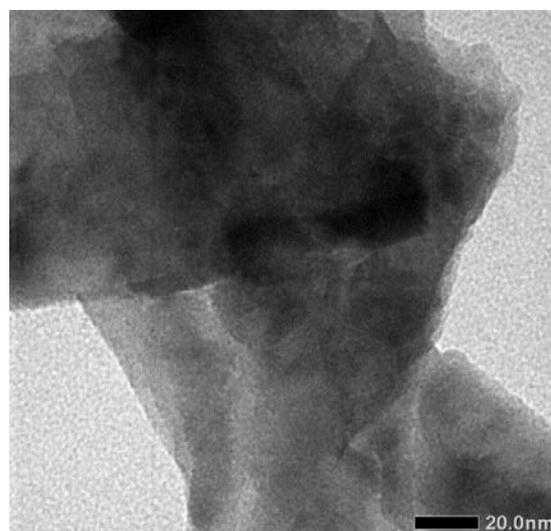


Fig.5 SEM images of the sample that sintered at 830°C in 10 minutes

The characterization of VSM obtained is a graph of the relationship between the external magnetic field (H) in units of Oe with the magnetization of the material (σ) in units of emu/g. The characterization using VSM aims to know the magnetic properties of the BSCNGO-2223 ($\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$) samples.

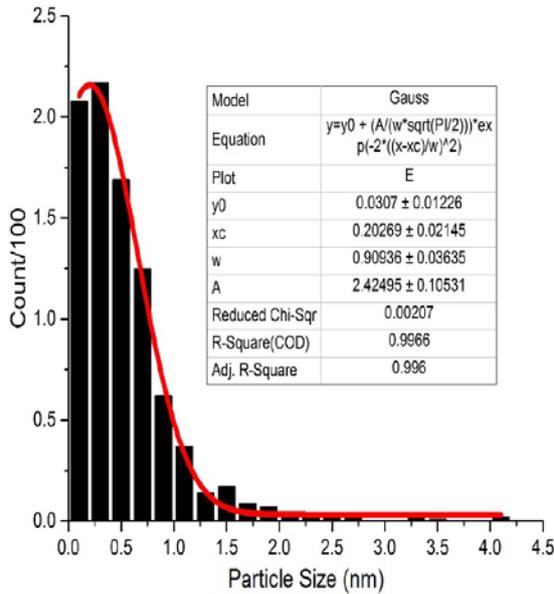


Fig.6 Particle size distributions of the sample that calcined at 450°C for 2 hours and 600°C for 1 hour

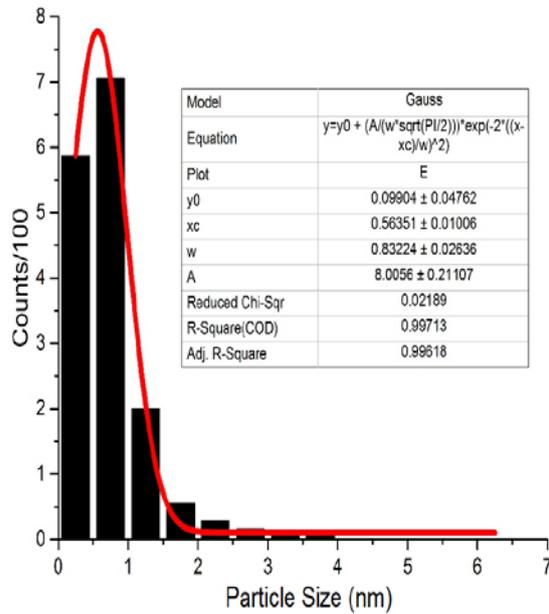


Fig.7 Particle size distributions of the sample that sintered at 830°C in 10 minutes

Characterization using VSM is done at room temperature. VSM characterization results can be seen in Figure 8 for the sample that calcined at 450°C for 2 hours and 600°C for 1 hour and Figure 9 for the sample that sintered at 830°C for 10 minutes. Both samples show the hysteresis curve indicating that the ferromagnetic properties appear at room temperature. With this result, it can be seen that the superconductor particles in nanometer size have ferromagnetic properties. This further confirms the predictions of Shipra et.al regarding superconductor particles in nanometer size will have ferromagnetic properties. From the results of the VSM data analysis (Table 3) shows that the larger the size of the crystal, the value of Ms increases, while the value of Mr. and Hc decreases.

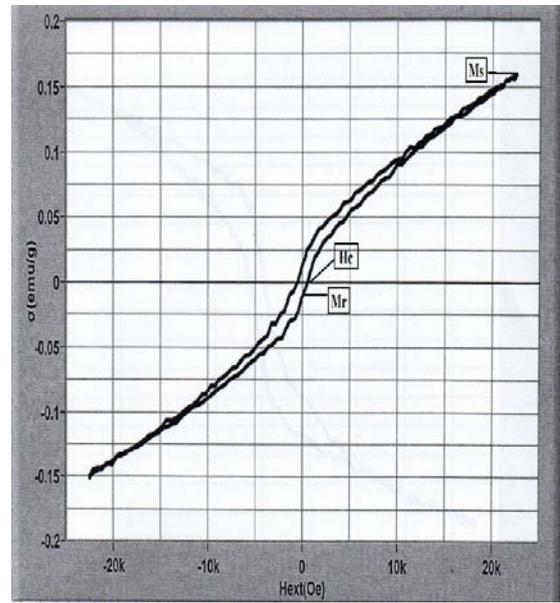


Fig.8 The curve of hysteresis of BSCNGCO (cal) samples

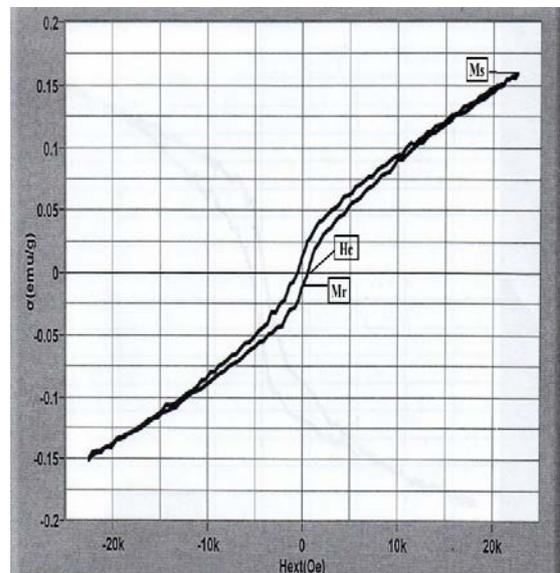


Fig.9 The curve of hysteresis of BSCNGCO (10) samples

Table 3. The value of M_s , M_r , and H_c of BSCNGCO sample

Sampel	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
BSCNGCO (Ca)	0.155	0.012	528.623
BSCNGCO (10)	0.157	0.011	476.327

4. CONCLUSION

From the research results can be concluded :

The increasing of the sintering time on $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors (10, 20 and 30 minutes) causes the increase of particle size (25.61, 26.20 and 30.08 nm).

The increasing of the sintering time on $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$ superconductors causes the decrease of the lattice parameter (a, b and c-axis).

The magnetic properties of the BSCNGCO ($\text{Bi}_2\text{Sr}_2(\text{Ca}_{1.5}\text{Nd}_{0.25}\text{Gd}_{0.25})\text{Cu}_3\text{O}_z$) superconductors are ferromagnetic.

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