Structural and superconducting aspects in $REBa_2Cu_3O_{7-\delta}$ (RE = Nd, Gd, Eu) superconductors prepared by wet-mixing method and varying sintering temperature

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Abstract. The rare-earth copper oxide superconductors of $Nd_1Ba_2Cu_3O_{7-\delta}$, $Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ and $Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3O_{7-\delta}$ have successfully been synthesized by introducing a wet-mixing method. Sintering was carried out at varying temperatures of 920, 940, 960 and 970°C for 10 hours in air. The effects of sintering temperature on the structural and crystallinity of the synthesized powders was studied using X-ray diffraction techniques. Rietveld analyses gave clearly separated diffraction (013) and (110) peaks at respectively 32.2° and 32.5°, decreasing Goodness-of-Fit, increasing average crystal size and increasing orthorhombicity with increasing sintering temperature from 920 to 970°C. In this research, the superconducting critical temperatures of $Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ and $Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3O_{7-\delta}$ powders sintered at 970°C and measured using a SQUID magnetometer was obtained to be about 88-91 K.

Keywords: *superconductor, wet-mixing method, X-ray, dc-susceptibility*

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INTRODUCTION

Synthesis of superconducting materials in order to obtain ones with high superconducting transition temperature *Tc*, high critical field *Hc* and high critical current *Jc* is still a challenge [1]. One of compounds representing strong candidate for practical applications is $RE_1Ba_2Cu_3O_{7-\delta}$ (RE denotes a rare earth element, RE-123), because it has a high critical current density *Jc* under a high magnetic field at 77 K [2, 3]. For these purposes, some researchers have attempted to synthesize superconductors by various processing methods and introducing various dopants. The RE-123 samples preparations using the sol-gel method [4], by the melt-textured growth [5], by infiltration-growth technique [6], and by top-seeded melt-growth (TSMG) [7] have so far been reported. Further, microstructure in conjunction with superconducting properties with various doping have also been investigated [8, 9].

This study is devoted to the effect of sintering temperature variations on RE-123 (RE=Nd, Eu, Gd) superconductors prepared by wet-mixing method. We introduced an acid solution as mixing media to achieve higher homogeniety of raw materials mixture, in order the sintering duration to induce further solid reaction is expected to be shorter for the significant high phase purity of RE-123. In this research, the only sintering temperature will be varied, while the duration is kept constant. The RE-123 (RE=Nd, Gd, Eu) samples synthesized were then examined using X-ray diffraction (XRD), scanning electron microscopy (SEM) and dc SQUID magnetometer.

EXPERIMENTAL

In this experiment, the superconducting $Nd_1Ba_2Cu_3O_{7-\delta}$, $Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ and $Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3O_{7-\delta}$ were synthesized from the starting materials of Nd_2O_3 (99.9%), Gd_2O_3 (99.9%) , Eu_2O_3 (99.9%), $BaCO_3$ (99.9%), and CuO (99.9%). All raw compounds were dissolved by HNO_3 solution, mixed and stirred until crusted and dried in oven at 100°C for 1 hour. The materials were heated in a furnace at 600°C for 3 hours, sintered at varying sintering temperature (920°C, 940°C, 960°C and 970°C) for 10 hours in ambient atmospere. The structure of the prepared powders was examined using powder X-ray (Cu*Kα* radiation, 10-90° 2θ-range with a step size of 0.02°) diffraction techniques (XRD).

Rietveld refinements of the obtained diffraction data were performed using *FullProf* [10]. SEM images of the sample were collected to determine the grain size. The magnetic susceptibility was measured with a Quantum Design SQUID magnetometer.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for $Nd_1Ba_2Cu_3O_{7-\delta}$ samples sintered at 920°C, 940°C, 960°C and 970°C for 10 hours, while Fig. 2 and 3 exhibit the XRD spectra for the samples with two combinations ($Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$) and three combinations ($Nd_{0.33}Eu_{0.33}Gd_{0.33}$ $Ba_2Cu_3O_{7-\delta}$) of rare-earth elements. According to these XRD spectra in the sense of diffraction angle, intensity, and peak patterns, all samples have generally been well crystallized with the dominant phase content to be the RE-123 phase. The changes in sintering temperature will affect the atomic diffusion process, leading to a change of reaction rate. The higher temperature induces the higher diffusivity. The lattice of $RE_1Ba_2Cu_3O_{7-\delta}$ samples with different sintering temperature (T_s) tends to be tetragonal at lower Ts and orthorhombic at higher T_s. The increasing sintering temperature has also affected more clearly the separated (013) and (110) diffraction peaks at 32.2° and 32.5° angles, as shown in Fig. 4-6. The important thing to mention in this matter, concerning the result of synthesis using the wet-mixing method, is that by sintering with much shorter duration we might obtain sample with somewhat higher phase purity compared to that obtained by dry-mixing with grinding technique [11] even for 10 hours.

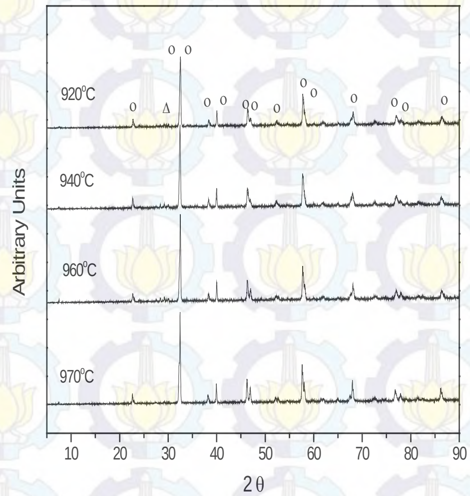

Figure 1. XRD patterns (CuKα radiation) of the $Nd_1Ba_2Cu_3$ $O_{7-\delta}$ with sintering temperature as specified. The present phases are indicated as (o)$Nd_1Ba_2Cu_3$ $O_{7-\delta}$, and (Δ) $BaCuO_2$

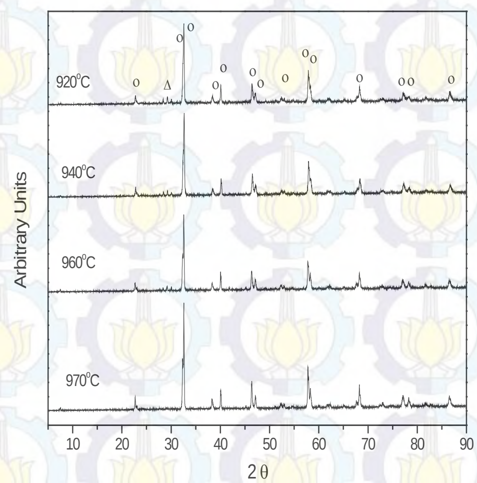

Figure 2. XRD patterns (CuKα radiation) of the $Nd_{0.5}Gd_{0.5}Ba_2Cu_3$ $O_{7-\delta}$ with sintering temperature specified. The present phases are indicated as (o)$Nd_{0.5}Gd_{0.5}Ba_2Cu_3$ $O_{7-\delta}$, and (Δ) $BaCuO_2$

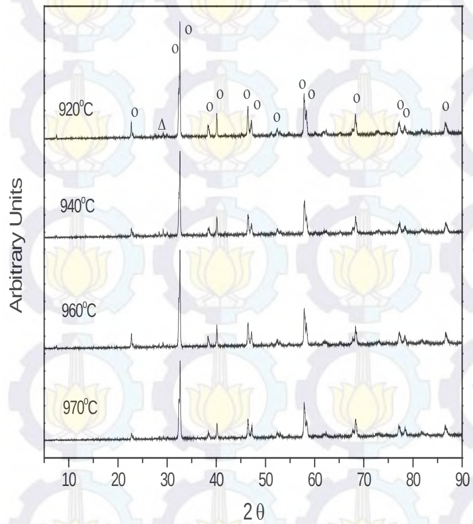

Figure 3. XRD patterns (CuKα radiation) of the $Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3O_{7-\delta}$ with sintering temperature specified. The present phases are indicated as (o)$Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3O_{7-\delta}$, and ($\Delta$) $BaCuO_2$

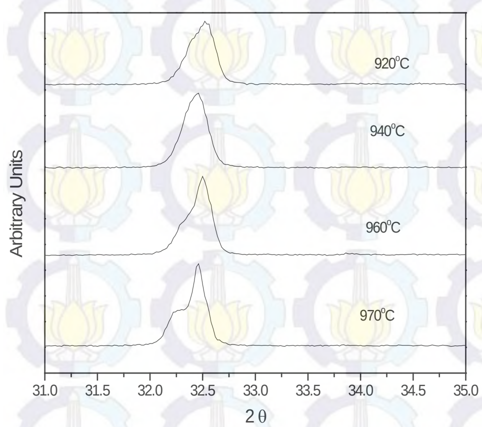

Figure 4. The (013) and (110) reflection peaks of the XRD patterns zoomed from Fig. 1

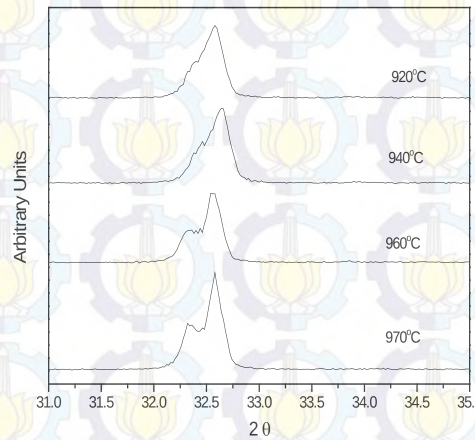

Figure 5. The (013) and (110) reflection peaks of the XRD patterns zoomed from Fig. 2.

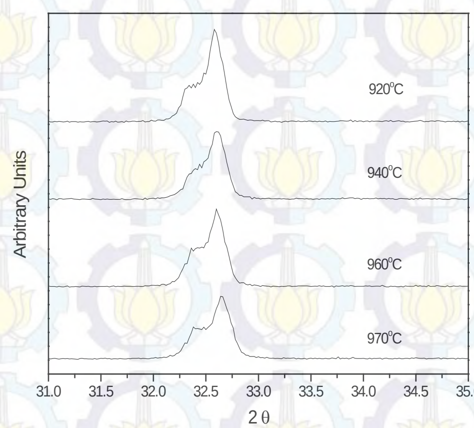

Figure 6. The (013) and (110) reflection peaks of the XRD patterns zoomed from Fig. 3

Going further regarding the 123-phase purity, one can see that in the XRD spectra for the diffraction angle between 27 and 32^o an impurity peak is observed which is associated with $BaCuO_2$ phase. This indicates that the initial mixing was still not perfect yet to result in a homogeneous mixture of cations needed for phase formation. This impurty content seems to be significantly reduced for the samples sintered at higher temperature. Meanwhile, the diffraction pattern refinement has conducted by Rietveld analysis method, employing the goodness-of-fit (GoF) or χ^2 to evaluate the curve fitness, as presented in Fig. 7. It can be explored from the figure that GoF decreases for samples sintered at higher temperature, signifying the better matching between the diffraction data and the model used for fitting. We can also estimate, additionally, the crystal size from the full-width-at-half-maximum of the diffraction peaks by using Scherrer equation. The crystal size of all samples increases with increasing sintering temperature in the range from 170 to 250 nm.

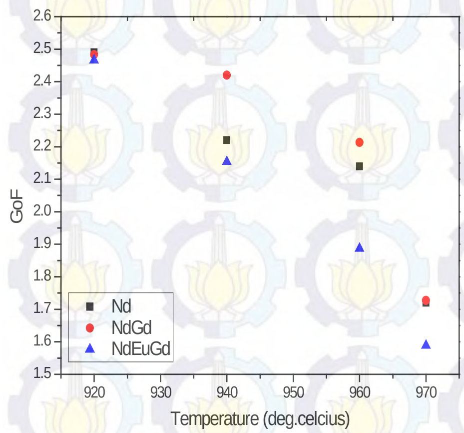

Figure 7. GoF at increasing sintering temperature of samples

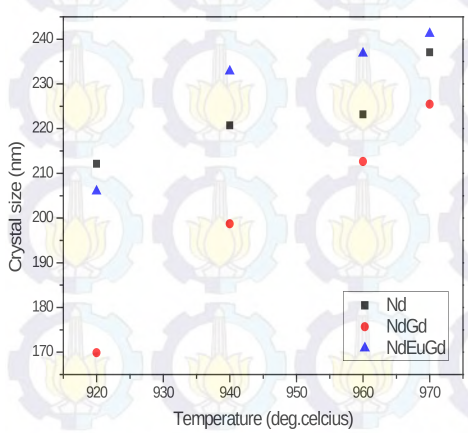

Figure 8. Crystal size vs. sintering temperature of samples

As stated above that the crystallographic lattice undergoes a tetragonal-orthorhombic phase transition for samples sintered from 920°C to 970°C. This phenomenon can correlate to the so-called orthorhombic strain η which is defined by: η = 2(b – a)/(b + a) as reported by Yang Li, et.al [12]. They have synthesized $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (x = 0-0.2) superconductors by solid state reaction, with calcined at 800°C for 24 h, pressed using 10^9 Pa, and sintered for 30 h, then annealed for 15 h. From their experiment, they demonstrated the crystallographic structure undergoing an orthorhombic-tetragonal phase transition from x = 0,06 to x = 0,18. Employing their experience, we arrive at the value of η for Nd-123, NdGd-123 and NdEuGd-123 samples, as shown in Fig. 9 and Fig. 10. The similar feature obtained in this experiment, where the crystallographic structure undergoes an orthorhombic-tetragonal phase transition from Ts = 920°C to Ts = 970°C. The orthorhombic strain increases with increasing sintering temperature (*thermal strain*) and the presence of other rare-earth elements (*doping strain*) in the 123-system.

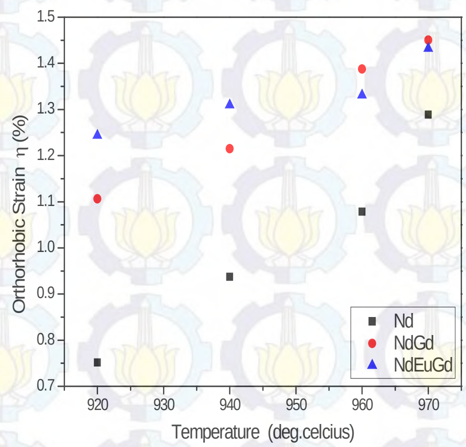

Figure 9. Orthorhombic strain for $RE_1Ba_2Cu_3O_{7-\delta}$

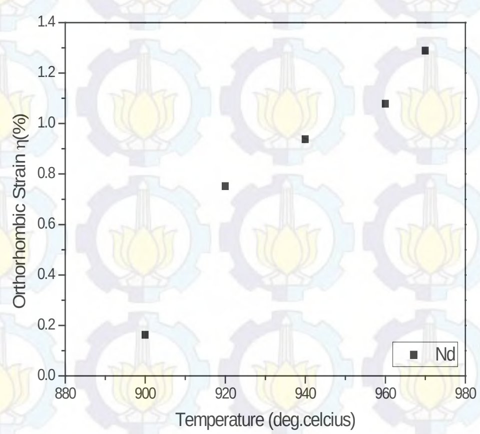

Figure 10. Orthorhombic strain for $Nd_1Ba_2Cu_3O_{7-\delta}$

Figure 11 de monstrates the dc magnetization, M(T) which have been presented to be normalized with magnetization at 10 K, M(10 K), of $Nd_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ and $Nd_{0.33}Eu_{0.33}Gd_{0.33}Ba_2Cu_3O_{7-\delta}$ samples sintered at 970°C in air. Both samples were shown to be superconducting respectively at 88 and 91 K. From zero-field cooling (ZFC) and field cooling (FC) curves, one may say that the presence of Eu element in the 123-system has led to the increasing superconducting critical temperature as well as stronger vortex pinning (by about 20%). Moreover, the SEM image $Nd_1Ba_2Cu_3O_{7-\delta}$ samples sintered at 920°C, 940°C and 970°C are shown in Fig. 12. These images displayed a homogeneous grain size and distribution in the samples with morphology representing the Nd-123 phase characteristics with average diameter in hundreds nanometer. The grain size clearly increases with increasing sintering temperature.

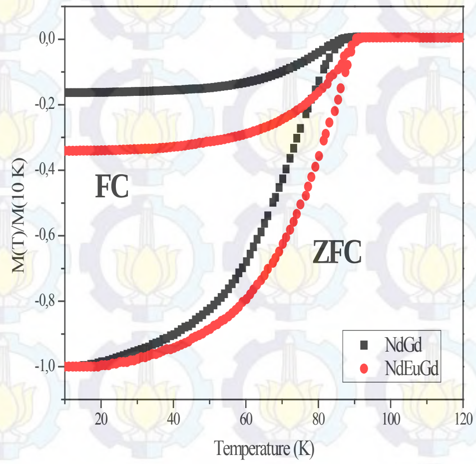

Figure 11. Temperature dependence magnetization of $RE_1Ba_2Cu_3O_{7-\delta}$

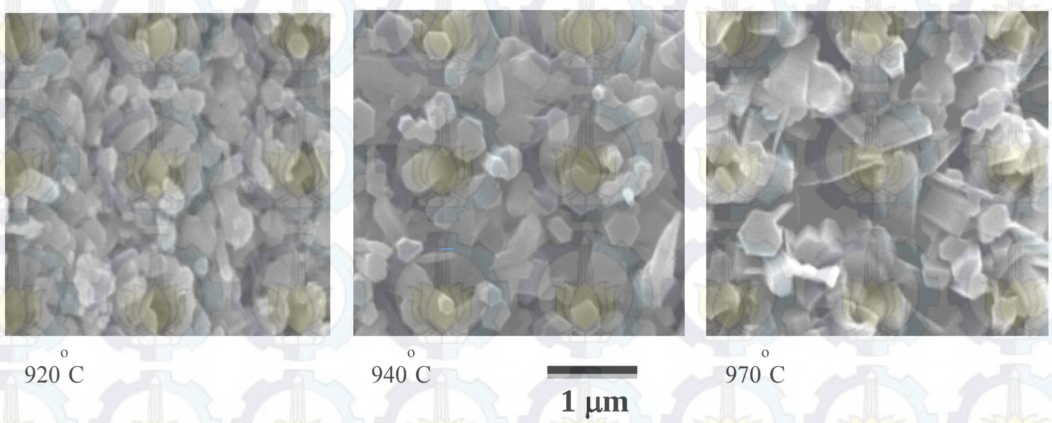

Figure 12. SEM images of $NdBa_2Cu_3O_{7-\delta}$ superconductor with sintering temperature as specified

CONCLUSION

The $RE_1Ba_2Cu_3O_{7-\delta}$ superconductor system, with RE = Nd, Gd and Eu, have successfully been synthesized by using wet-mixing method, resulting significantly high phase purity. The increasing temperature of sintering has led to improvement of crystallinity, represented among others by the separated (013) and (110) diffraction peaks at 32.2° and 32.5° angles, the reducing impurity and decreasing GoF. This sintering process together with the presence of doping (Gd and Eu) in the Nd-123 system has enhanced the orthorhombic strain, superconducting critical temperature and vortex pinning in field cooling.

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