Effect of Substitution Sr Cations on the Structure in the Gd$_1$(Ba$_{2-x}$Sr$_x$)Cu$_3$O$_{7-\delta}$ Phases

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Abstract

In an effort to improve the performance of superconductors in the field and high temperatures it is important to study the superconducting mechanism. For this reason, the cation substitution can be conducted. One of the high Tc superconductors Gd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase with Sr substitution has been synthesized, i.e. Gd$_1$(Ba$_{2-x}$Sr$_x$)Cu$_3$O$_{7-\delta}$ compound. The sample was synthesized by using a solid-state reaction method with a wet mixing, sintered for 12 hours at temperature 900°C. The synthesis results are characterized by using XRD. The results of Match-3 software analysis showed high (higher 85%) Gd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ phase was formed. The Sr substitution causes changes to the structure, i.e. the lattice parameters $a$, $b$ and $c$, where the orthorhombicity tends to decrease with increasing Sr content. Refinement results show that based on the oxygen occupancy, the total oxygen content tends to increase.

Keywords

Wet Mixing, Gd$_1$(Ba$_{2-x}$Sr$_x$)Cu$_3$O$_{7-\delta}$ Compound, Sr Substitution, Lattice Parameters, Orthorhombicity

1. Introduction

One of the superconducting materials with high critical temperatures that have been successfully discovered is the Gd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ (GBCO-123 system) with a critical temperature of 94 K by Yamaguchi, 2014 [1] so it is very possible to be utilized with liquid nitrogen cooling. However, the GBCO-123 superconductor has Tc and Jc which are still strongly influenced by magnetic fields [2]. Therefore, research is still needed to improve the performance of the superconductor in high temperatures and high magnetic fields.

In this research substitution of Ba was carried out, i.e. Sr in the Gd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ superconductor system with the chemical formula Gd$_1$(Ba$_{2-x}$Sr$_x$)Cu$_3$O$_{7-\delta}$. The se-
lected Sr element refers to the results of research from Zhuo, 1999 [3], the effect of Sr substitution on Ba in the Hg_{0.7}Pb_{0.3}Ba_2Ca_2Cu_3O_{y} superconductor. Sr substitution of Ba can cause a decrease in lattice $c$ parameter of 0.7 Å. It was found that the irreversibility line for Sr substituted compounds shifted towards higher temperatures compared to pure samples without Sr. From analysis of the reversible magnetization, it shows that the magnetization fluctuation is much reduced, and the interlayer-coupling magnetization strength can be increased. The critical field over $H_{c2}$ is almost twice compared to pure samples without Sr.

The effect of Sr substitution on superconductivity, especially the hole doping mechanism in the Hg_{x}(Ba_{1−y}Sr_{y})_{2}YCu_{2}O_{8−δ} system has been investigated by Toulemonde et al. [4]. It was explained that it was possible to increase $T_c$ from 0 K for $y = 0$ to 42 K for $y = 1.0$. The distribution of charge between the cell unit atoms shows the transfer of charge into the CuO$_2$ plane through two doping, i.e. through O(2)-Cu and Ba/Sr-O(1) bonds respectively. In research conducted by C.H. Chin et al. 2003, substitution of Gd with Ca and Sr has been carried out [5]. The relationship between $T_c$ and orthorobicity and $\angle$O(1)-Ba-O(1) angles along the a-axis has been explained.

In this study, Sr substitution was carried out in the GBCO-123 system phase in relation to the doping impact of Sr in the formation of the Gd$_1$Ba$_2$Cu$_3$O$_{7−δ}$ phase. To get a homogeneous mixture in the study a wet mixing method using nitric acid as a solvent is used.

2. Experiment Method

In the synthesis of Gd$_{x}$(Ba$_{2−x}$Sr$_{x}$)Cu$_2$O$_{7−δ}$ compounds, the Gd$_2$O$_3$, SrO, BaO and CuO powder materials with purity > 99.9% and HNO$_3$ with purity 65% (Sigma-Aldrich)are used. The Gd$_{x}$(Ba$_{2−x}$Sr$_{x}$)Cu$_2$O$_{7−δ}$ compounds having compositions of $x = 0.0, 0.05, 0.15, 0.25$ and $0.5$ were prepared by the solid state reaction methods, mixing is done by a wet-mixing method using HNO$_3$ according to previous research [6]. After the powder was weighed according to the stoichiometric composition then mixed in 100 ml of HNO$_3$, stirred using a magnetic stirrer for 24 hours. The mixture is then heated at 250°C to form a crust. The sample mixture is then crushed in a mortal and calcined in a furnace at 400°C for 2 hours, continued at 500°C for 2 hours and finally at 600°C for 6 hours. After grinding the sample is heated at 900°C for 15 minutes. The results are crushed and then molded into pellets with a hydraulic press at 500 Pa pressure on a 1.5 cm diameter mold. The pellets are sintered according to the atmosphere in the furnace for 12 hours at 900°C. The sample is cooled according to cooling in the furnace.

The sample was characterized by XRD at an angle of 2θ = 50° - 60°, the existence of the Gd$_1$Ba$_2$Cu$_3$O$_{7−δ}$ phase was analyzed by using Match-3.6.1.115 Software. Identification of the diffraction peaks of experiment result matched with reference entry number 96-153-9606 with formula Gd$_1$Ba$_2$Cu$_3$O$_7$ from COD-Inorg REV211633 2018.10.25 was used. For analyzing the changes of structural Rietica software was used.
3. Results and Discussion

The X-ray spectra of RBa$_2$Cu$_3$O$_{7-δ}$ are in general similar to the yttrium analogs [7]. Figure 1 is the XRD diffraction spectrum pattern of Gd$_x$Ba$_{2-x}$Sr$_x$Cu$_3$O$_{7-δ}$ phase for $x = 0$, 0.05, 0.15 and 0.25. The results match of the XRD experiment and reference number entry 96-153-9606, peaks diffraction of Gd$_x$Ba$_{2-x}$Sr$_x$Cu$_3$O$_{7-δ}$ phase has been identified. Amount (in %) of the identified the peaks area that match as Gd$_x$Ba$_2$Cu$_3$O$_7$ phase shown in Figure 2, shows that the increase of Sr content does no significant differences. For all of samples amount are more than 85%, this indicates that a single-phase not yet reached. This may be related to the higher melting point of SrO compared to BaO, i.e. 2531˚C and 1923˚C respectively. It is cause a shift in the reaction temperature (sintering) of the Gd$_x$Ba$_{2-x}$Sr$_x$Cu$_3$O$_{7-δ}$ phase formation to at higher temperatures.

Differential Thermal Analysis (DTA) in flowing air was carried out on the precursor powder with a heating rate 10˚/minute to investigate the sintering temperature for Gd$_x$Ba$_{2-x}$Sr$_x$Cu$_3$O$_{7-δ}$ phase formation. The DTA characterization results for Gd$_x$Ba$_{1.95}$Sr$_{0.05}$Cu$_3$O$_{7-δ}$ as shown in Figure 3. From Figure 3, peak at temperature 920˚C and 1038˚C was observed. According some researchers previously it is shown that the Gd$_x$Ba$_2$Cu$_3$O$_7$ phase can formed at temperatures between 900˚C - 950˚C [7] [8] [9]. As a result Figure 3 suggests that a temperature at temperature 920˚C represents the chemical reaction temperature (sintering temperature) for formation of the Gd$_x$Ba$_{1.95}$Sr$_{0.05}$Cu$_3$O$_{7-δ}$ phase. The YBCO-123 family superconductor has a peritectic temperature at temperatures between 980˚C - 1090˚C [10] [11] [12]. The endothermic DTA peaks under oxygen corresponding to the peritectic melting reaction which takes place at...
1073°C [13] and the peritectic temperature of GBCO-123 bulk superconductors, i.e. 1030°C [14]. Therefore we suggest that a temperature at 1038°C represents the peritectic melting reaction temperature for the Gd$_1$Ba$_{1.95}$Sr$_{0.05}$Cu$_3$O$_{7-δ}$.

Analyses of the X-ray diffraction data was conducted by using the orthorhombic structural with Pmmm (47) space groups by the Rietveld structural refinement to obtain structural parameters. This is carried out by Rietica program. Refinements results shows the good of fitness (GOF) = 1.69, 2.57, 2.64, 3.17 and 2.78 for Sr content $x$ = 0.00, 0.05, 0.15, 0.25 and 0.50 respectively. The refinement results, the value of $a ≠ b < c$ were obtained, so that Gd$_{1-2x}$Sr$_x$Cu$_3$O$_{7-δ}$ phase is in the orthorhombic structure. The changes of the lattice parameters for Sr substitution are as given in Figure 4.

In Figure 1, the peaks in the four main regions of the Bragg angle $2θ$ around 32° to 33°, 38° to 39°, 45° to 49°, 57° to 60° [7] [15] was indexing according diffraction from Gd$_1$Ba$_2$Cu$_3$O$_7$ phase. In Figure 1, the main diffractions showing
The changes in the Gd$_{1}$Ba$_{2-x}$Sr$_{x}$Cu$_{3}$O$_{7-δ}$ phase cell parameters are: (013) and (103) at $2θ = 32° - 32.8°$, (020) and (200) at $2θ = 46° - 47.5°$, and (123) and (213) at $2θ = 57.5° - 59°$. Each pair of the above diffractions is accompanied by additional overlapping reflections (110), (006) and (116), respectively. The splitting of these diffractions peaks indicates changes in the orthorhombicity of the unit cell [15]. This is correlation with changes of the lattice parameter $a$, $b$, and $c$ as shown in Figure 4.

From Figure 1, for samples with $x = 0.05 - 0.25$ at an angle $2θ$ between $46.5° - 47.5°$ the diffraction planes (200) and (020) appear clearly separated, each at an angle of $2θ = 46.84°$ and $47.14°$. This indicates that the Gd$_{1}$Ba$_{2-x}$Sr$_{x}$Cu$_{3}$O$_{7-δ}$ phase formed is in the orthorhombic cell unit. Meanwhile, samples with $x = 0$ and 0.05, the separation between the diffraction planes (200) and (020) appear to shrink, this gives an indication that the Gd$_{1}$Ba$_{2-x}$Sr$_{x}$Cu$_{3}$O$_{7-δ}$ phase formed is still orthorhombic but with smaller in the orthorhombicity (Figure 7).

As shown in Figure 4 in a range $x = 0 - 0.25$, the lattice constants of $a$, $b$ and $c$ trend to changes towards smaller sizes with the increasing Sr elements content. But the decreases lattice parameter of $b$ is relatively more slowly compared the changes of $a$, therefore the changes of orthorhombicity take place. The changes can be understood from the size effect and oxygen redistribution along $a$ and/or $b$-direction [16].

Size of the ionic radii of Ba and Sr elements are different, i.e. Ba$^{2+}$ and Sr$^{2+}$ having ionic radius sizes of 1.49 Å and 1.32 Å respectively, but have the same valence state [17]. Because the ionic radius of Sr$^{2+}$ is smaller, substitution of Ba with Sr causes the three lattice parameters $a$, $b$ and $c$ to be decreased with increasing Sr content. The decreases give an indication that Sr elements have entered the Ba-site. This is according to increasing Sr content in the cases of cation substitution on YBCO-system superconductors as given in [18] [19] [20].

Figure 4. The changes of lattice constants in different Sr contents in the Gd$_{1}$Ba$_{2-x}$Sr$_{x}$Cu$_{3}$O$_{7-δ}$.
From Figure 4, reveals there a little different of the decrease of lattice parameters of \(a\) and \(b\) for range \(x = 0 - 0.25\). While for Sr content of \(x > 0.5\), lattice constants of \(a\) and \(b\) increases but with different gradient. The different of changes may be correlated with different distribution oxygen along \(a\)-direction and \(b\)-direction. According to orthorhombic and tetragonal structures in reference 21, from refinement results, the occupancy for O(1)-site and O(5)-site are \(n_{O(1)}\) and \(n_{O(5)}\) respectively as shown in Figure 5. It reveals that in range of \(x = 0 - 0.2\) oxygen occupancy for O(1)-site along \(b\)-direction is relatively constant, while the O(5)-site along \(a\)-direction decreases. Therefore, the changes in the lattice parameter of \(a\) and \(b\) noting same. The large amount of Sr\(^{2+}\) substituting for Ba\(^{2+}\) results in contract stress around B-site. For keep a balance structure inner stress must be produced. For this reason redistribution oxygen at O(5)-site and oxygen at O(1)-site. In this case occupancy oxygen on O(5)-site conducted so that the difference occupancy oxygen at O(1)-site and O(5)-site became smaller and reduces of the orthorhombicity occurred as shown in Figure 7. From the refinement results, the total oxygen as given by the sum of the occupancy parameters [19], i.e.

\[
y = n_{O(1)} + n_{O(5)}
\]

where \(n_{O(1)}\) and \(n_{O(5)}\) are occupancy for O(1) and O(5) site respectively The calculation results of Equation (1) as shown in Figure 6. From this figure can be shown that oxygen content decreases in range Sr content of \(x = 0 - 0.25\) and then increases for \(x > 0.25\).

From Figure 4 it appears that there are significant differences the lattice parameters values of \(a\) and \(b\), indicating that the GdBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) phase doped Sr has an orthorhombic structure. The relative changes of the lattice constants of \(a\) and \(b\) can be recognized from orthorhombicity splitting which is defined [15],

\[\text{Figure 5. The change of occupancy for O(1)-site and O(5)-site.}\]
Figure 6. The oxygen content in Sr variation on Gd$_{(1-x)Sr}$Cu$_3$O$_{y}$ compound.

Orthorombicity splitting \[ \frac{b-a}{a+b} \times 1000 \] (2)

The calculate results theorthorombicity splitting by using Equation (2) as shown in Figure 7 were obtained. It appears with Sr content increases that the orthorombicity of the Gd$_{(1-x)Sr}$Cu$_3$O$_{7-\delta}$ phase is changes. First, from \( x = 0 - 0.05 \) orthorombicity increase, then in range \( x = 0.05 - 0.25 \) decreases and for \( x > 0.25 \) decrease more sharply take place. In the range of \( x = 0.05 - 0.50 \) the changes of lattice constants \( a \) and \( b \) diminish the orthorombicity. However, all the added samples are conserved with the orthorhombic structure similar to the pure sample and no orthorhombic-to-tetragonal transition occurs.

The changes lattice parameters of \( a, b \) and \( c \) indicate there are the changes in unit cell volume. The unit cell volume dependence of Sr content, as shown in Figure 8, reveals that the unit cell volume is decreases with increasing Sr content. For range on \( x = 0 - 0.5 \) the total decrease about 1.7%. The variation in lattice parameters \( (a, b, c) \) and unit cell volume with increasing Sr concentration show that Sr$^{2+}$ may be incorporated into the crystal structure of the Gd$_{(1-x)Sr}$Cu$_3$O$_{7-\delta}$ phase, the cation of Sr occupy the Ba -sites. The pattern changes of the cell unit volume almost to resemble a pattern the changes in oxygen content as in Figure 6. It indicates that the cation substitution of Sr may result in a change of the oxygen-content in Gd$_{(1-x)Sr}$Cu$_3$O$_{7-\delta}$ phase. Therefore, the changes of the unit cell volume giving an indication of the changes in oxygen content in the crystalline structure of Gd$_{(1-x)Sr}$Cu$_3$O$_{7-\delta}$ phase, which is another factor that affects the lattice constant [21] [22].

4. Summary

In the synthesis of Gd$_{(1-x)Sr}$Cu$_3$O$_{7-\delta}$ phase compounds, the Sr element can replace the Ba element. The refinement results, for \( x = 0, 0.05, 0.15, 0.25 \) and \( 0.50 \) the value lattice parameters of \( a \neq b < c \) were obtained, so that Gd$_{(1-x)Sr}$Cu$_3$O$_{7-\delta}$ phase is in the orthorhombic structure. The increasing Sr content causes the
Figure 7. The orthorombicity in different Sr contents in the Gd$_1$Ba$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$.

Figure 8. Changes in the volume of cell units due to increased content of Sr.

changes lattice parameters of $a$, $b$ and $c$. In the range of $x = 0.05 - 0.50$ the changes of lattice constants $a$ and $b$ diminish the orthorhombicity. However, all the samples are conserved with the orthorhombic structure and no orthorhombic-to-tetragonal transition occurs.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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