EFFECT OF FLUORINE ON SOME PROPERTIES OF Y235 SUPERCONDUCTOR

T. KRUAEHONG[a*], T. KHUNTAK[b], P. CHAINOK[c], S. SUJINNAPRAM[d], T. NILKAMJON[e], S. RATRENG[f], P. UDOMSAMUTHIRUN[g]
[a]*Department of Physics, Faculty of Science and Technology, Suratthani Rajabhat University, Surat Thani 84100, Thailand.*
[b]*The Institute for the Promotion of Teaching Science and Technology, Sukhumvit Road, PhraKhanong, Bangkok 10110, Thailand.*
[c]*Department of Science and Mathematics, Faculty of Science and Technology, Pathumwan Institute of Technology, Bangkok 10330, Thailand.*
[d]*Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University, KamphaengSaen Campus, Nakhon Pathom 73140, Thailand.*AND
[e]*Prasarnmit Physics Research Unit, Department of Physics, Faculty of Science, Srinakharinwirot University, Bangkok 10110, Thailand.*AND
Thailand Center of Excellence in Physics(ThEP), Si Ayutthaya Road, Bangkok 10400, Thailand.
[f]*Prasarnmit Physics Research Unit, Department of Physics, Faculty of Science, Srinakharinwirot University, Bangkok 10110, Thailand.*AND
Thailand Center of Excellence in Physics(ThEP), Si Ayutthaya Road, Bangkok 10400, Thailand.
[g]*Prasarnmit Physics Research Unit, Department of Physics, Faculty of Science, Srinakharinwirot University, Bangkok 10110, Thailand.*AND
Thailand Center of Excellence in Physics(ThEP), Si Ayutthaya Road, Bangkok 10400, Thailand.

The purpose of this research aims to study the physical properties of the Y123 and Y235 superconductor doped fluorine by solid state reaction.The conventional process with the calcination temperature at 810 °C and the sintering temperature at 925 °C were done. The samples obtained with optimal doping had the highest critical temperature at 95 K and 93 K for Y123 and Y235, respectively. There was no effect of doping on lattice parameters but the anisotropy parameter of Y235 was dependent on fluorine doping. The iodometric titration method was done that the pure Y123 and Y235 were shown the highest of Cu^{3+}/Cu^{2+} ratio and deficiency parameter. We also found the highest amount of Cu^{3+}/Cu^{2+} ratio at the optimal fluorine doping.

(Received January 20, 2016; Accepted March 22, 2016)

Keyword: superconductor, solid state method, critical temperature, Y235, fluorine doped.

1.Introduction

The superconducting oxide of the $YBa_2Cu_3O_{7-x}$ (Y123) is attraction for application[1,2] because the first superconductor having critical temperature (T_c) more than the boiling point of liquid nitrogen. The superconductor synthesized by Chu and co-workers[3] in 1987, The critical temperature about 92 K with the orthorhombic perovskites crystal structure of Y123. The CuO_2 planes play an important role of superconductivity but CuO chains play as non-superconducting[4].The increasing in the oxygen content in the CuO_2 plane induced to occur the orthorhombic to tetragonal transition which the tetragonal structure are in non-superconducting

* Corresponding author: kruaehong@hotmail.com

phase. During the past twenty years, researchers have been investigating and found that the Y-based superconducting compounds as Y123, $YBa_2Cu_4O_8$(Y124) and $Y_2Ba_4Cu_7O_{15}$(Y247). The T_c of Y124 and Y247 were at 80 K[5]and 40K[6], respectively. However, oxygen content has an effect on critical temperature of the Y247 superconductor; T_c ranges from 30 K to 95 K[7,8]. In 2009, new superconductor Y358 ($Y_3Ba_5Cu_8O_{18}$) was synthesized by solid state reaction[9,10]with a T_c above 100 K, and the lattice parameters are *a*=3.888 Å, *b*=3.823 Å, *c*=31.013 Å. In 2010, Udomsamuthirunet al.[11]found new YBaCuO superconductors i.e.,Y5-6-11, Y7-9-16, Y5-8-13, Y7-11-18, Y1-5-6, Y3-8-11 and Y13-20-33. These superconductors were synthesized by using the assumption that the number of CuO_2 planes and CuO chains are related to the number of Ba-atom and Y-atom.The number of Ba-atom plus Y-atom are equal to the number of Cu-atom. However, their critical temperatures were in the same range of Y123. In 2011, Topal and Akdogan[12]also synthesized and characterized three new YBaCuO superconductors i.e., $Y_2Ba_3Cu_{5.2}O_y$ (Y2352), $Y_2Ba_5Cu_9O_y$(Y259), and $Y_1Ba_4Cu_5O_y$ (Y145). The $T_c$onset was determined to be 98 K, 98 K, and 97.3 K for Y-2352, Y-145, and Y-259, respectively. The X-ray analysis showed their structures were in Y123 phases. Chainok et al.[13] synthesized and characterized the physical properties of Y123 and $Y_1Ba_4Cu_5O_y$(Y145) superconductors by solid state reaction in the air atmosphere with sintering temperature at 950 °C and 980 °C.The crystal structure of Y145 was orthorhombic which *a* = 3.800 Å, *b* = 3.860 Å and *c* = 19.370 Å and the peritectic temperature at 1,018 °C.

One of the methods used to increase the critical temperature,“doping” superconductor by adding materials affecting on the ratio of Cu^{2+}/Cu^{3+}.The ratio of trivalent copper of Y123 ($YBa_2Cu_{2x}{}^{3+}Cu_{3-2x}{}^{2+}O_{6.5+x}$) with the $T_c$onset = 60 K (x= 0.23), 90 K (x = 0.35) and non-superconductor ($x\approx$ 0) were investigated by Choy et al.[14]; The result found that the ratio of Cu^{3+}/Cu^{2+} depend on the annealing temperature and period of time.The highest T_c is Cu^{3+}/Cu^{2+}. Dong Han Ha et al.[15] studied the effects of cation substitution, Sr and Ca, on the oxygen loss in YBaCuO superconductors, The result found that the oxygen is removed more easily by increasing Ca concentration due to the displacement of Ba ions from the Cu-O chain towards the CuO_2 plane. The oxygen content at y= 6.96 for $YBa_2Cu_3O_y$, $T_c\approx$ 92K. Mazaheri, Ghasemi and Heidarpour[16]synthesized Y257($Y_2Ba_5Cu_7O_x$) superconductor by solid state reaction at ambient pressure.The samples were calcined and sintered at 850°C with the cooling part in three steps at 650°C, 600°C and 550 °C for 10 hrs each. The electrical measurements were investigated in the 60-300 K temperature range with the presence of magnetic field. The result found that the $T_c$offset and the $T_c$onset were at 92 K and 98 K, respectively.

The fluorine is one of the candidates for doping a superconductor to increase the critical temperature[17]. Since 1987, Ovshiskyet al.[18,19] had reported Y123 doped with fluorine had a T_c about 155 K. They used Y_2O_3, $BaCO_3$, CuO and BaF_2 as starting materials with firing in air at 950°C for 8 hrs. In 2011, Srivasanet al.[20] synthesized Y358 doped with fluorine it has T_c about 110 K. The powders of Y_2O_3, $BaCO_3$, CuO, and CuF_2 were mixed in appropriate stoichiometric ratio. The samples were calcined inair at 810°C, sintered at 950°C and at 925°C. Recently, Kruaehong[21] investigated the effect of the fluorine doping on Y123, Y358 and Y3-8-11 bulk superconductors. The CuF_2 was used as doping material. The results revealed that $T_c$onset and $T_c$offset were decreased when the fluorine doping was increased because the calcinations temperature above peritectic temperature of fluorine, the fluorine decomposition and deplete superconductivity.

In this research, aim to study the physical properties of Y235($Y_2Ba_3Cu_5O_x$) doped fluorine($Y_2Ba_3Cu_5O_{y-x}F_x$) superconductors prepared by solid state reaction. The calcination temperature at 810 °C and the sintering temperature at 925 °C had been done. All samples were characterized by the SEM, EDX, XRD with Rietveld full-profile analysis, the Iodometric titration and the resistivity measurement.

2. Experimental process

The pellets of Y123 and Y235 superconductors doped fluorine were synthesized by solid state reaction. The powder of Y_2O_3, $BaCO_3$, CuO and CuF_2 were mixed and ground in stoichiometric ratios that Y123+F_x and Y235+F_x ; x=0, 0.05, 0.10, 0.15, 0.20 and 0.25.The calcinations process was done twice time in air at 810 °C for 24 hrs and increase to 925 °C for 1 hr. The powders was pressed to pellets of 30 mm diameter with mold. The sintering process was in air at 925 °C for 24 hrs and then annealing at 500 °C for 24 hrs in oxygen atmosphere to ensure complete oxygenation.The samples were synthesized by using calcinations temperature at 810 °C which was in the range of the peritectic temperature of CuF_2 that about 836 °C[22]. All samples were characterized by the SEM micrograph and EDX (JEOL, JSM 6400), the XRD (Bruker D8-Discovery diffractometer). The oxygen content was characterized by iodometric titration. The resistivity measurements were performed with four point-probes techniqueand the crystal structures were performed by Rietveld full-profile analysis method. Energy Dispersive Spectroscopy (EDS) analysis was carried out to investigate stoichiometry and chemical composition.

3. Results and Discussion

The SEM micrograph and EDX showed that the micrographs of samples with fluorine doping were larger grain size and less porosity than the others, whereas the grains in the samples were randomly oriented and the EDS spectrum revealed. The consisted of sample with Y, Ba, Cu, O and F without impurity.

The DC-four point probes were used for resistivity measurement versus temperature between 77 K to 120 K. The normalized resistivity versus temperature of $Y123+F_x$ and $Y235+F_x$ which x=0, 0.05, 0.10, 0.15, 0.20, and 0.25 were shown in Fig.1(a) and Fig.1(b), respectively. The summations of critical temperature onset were shown in Table 1. The effect of F-doping on the critical temperature was shown in Figure 2. The bell shaped curvewas found in both Y123 and Y235.The maximum critical temperature onset were found at x =0.1 that of Y123 at 95 K and Y235 at 93 K.

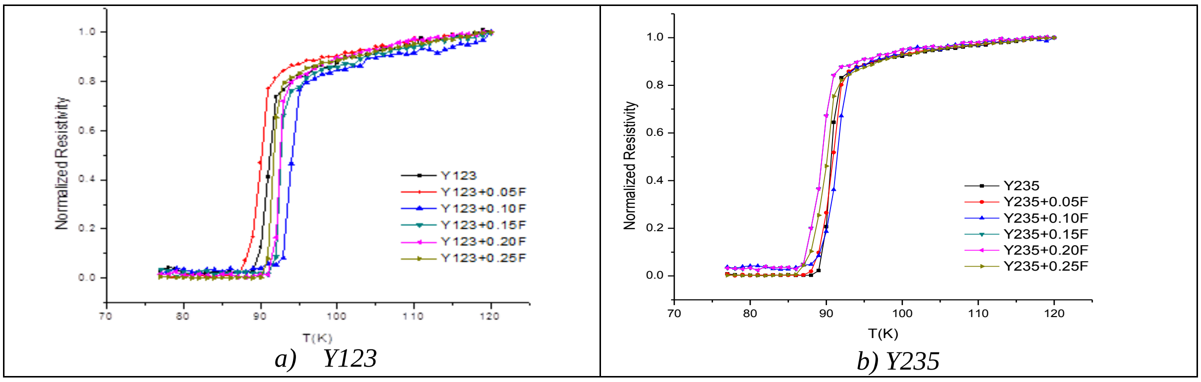

Fig.1.This is the critical temperature in the resistivity measurement of Y123(a) and Y235(b).

Table 1.This is the critical temperature of the samples of fluorine doped.

Sample	T_{offset} (K)	T_{onset} (K)
YBa_2Cu_3O	89	92
$YBa_2Cu_3O_{y-0.1}F_{0.05}$	87	91
$YBa_2Cu_3O_{y-0.1}F_{0.10}$	93	95
$YBa_2Cu_3O_{y-0.1}F_{0.15}$	91	94
$YBa_2Cu_3O_{y-0.1}F_{0.20}$	91	94
$YBa_2Cu_3O_{y-0.1}F_{0.25}$	90	93
$Y_2Ba_3Cu_5O_y$	89	92
$Y_2Ba_3Cu_5O_{y-0.1}F_{0.05}$	88	93
$Y_2Ba_3Cu_5O_{y-0.1}F_{0.10}$	88	93
$Y_2Ba_3Cu_5O_{y-0.1}F_{0.15}$	87	92
$Y_2Ba_3Cu_5O_{y-0.2}F_{0.20}$	87	92
$Y_2Ba_3Cu_5O_{y-0.2}F_{0.25}$	86	92

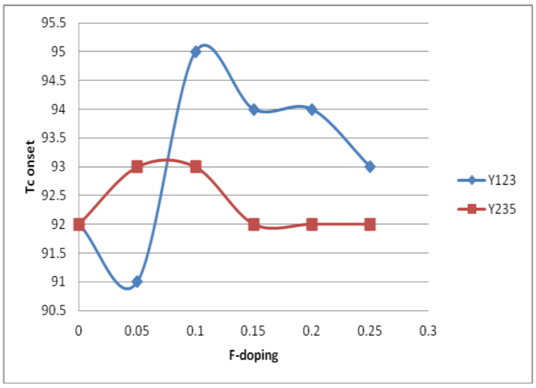

Fig. 2. This is the effect of F-doped on the critical temperature.

According to Table 1.and Fig.1 and 2., The Fluorine doped samples with x=0.1 shown the highest critical temperature. The later value, the critical temperature tends to decrease. This result was consistent with the research of Ovshisky et al. [18,19] and K.srivasan et al.[20] that studied on the effect of Fluorine doped on the critical temperature of Y123 and Y358 superconductor. However in this research the samples were synthesize by using calcinations temperature at 810 °C which was in the range of the peritectic temperature of CuF_2 about 836 °C[22]. The calcinations temperature was less than of conventional method about 950 °C so that would occur the non-complete solid state reaction in our samples. This result consist of the analysis from X-ray diffraction that found both superconducting compound and non-superconducting compound.

For the powder X-ray diffraction analysis, the pellets were reground to fine powder and then XRD analysis was carried out. The X-ray diffraction patterns taken at room temperature in over the range 2θ= 10°– 90° with CuK_{α} radiation. The Fullprof software were used for characterizing the crystal structure profile. The study found that, there were two compositions in our samples; superconducting compound and non-superconducting compound. For Y123, the non-superconducting compound was Y211 (Y_2BaCuO_5) with Pbnm space group. For Y235, the non-superconducting compounds were $BaCuO_2$ and $Ba_2Cu_3O_6$ with Im-3m and Pccm space group, respectively. The superconducting phase was increased with the F-doping concentration.

The crystal structures of superconducting compounds were orthorhombic structure[23-25]with Pmmm space group[26]. The increasing of F-doping was no significant, change in *a*-axis value and *b*-axis values which the lattice parameters of *a*=3.82184Å, *b*= 3.88439Å and *c*=11.66411Å:Y123 and *a*= 3.82025 Å, *b*=3.86825Å and *c*=18.92999Å:Y235 as shown in Figure 3. The possible found that the during cooling process in the air, the fluorine in the sample evaporates and the fluorine has an oxidative materials[27]. However, the effect on anisotropy were found in Y123 but little effect on Y235. The anisotropy was about 1.8 for Y123 but depend strongly on F-doping for Y235, the highest was about 2.5 and the lowest was about 1.25. Because the crystal structure of Y235 has *c*-axis more than Y123 as a result; the crystal structure more vibration more easily than Y123 cause anisotropy of Y235 has many different value.

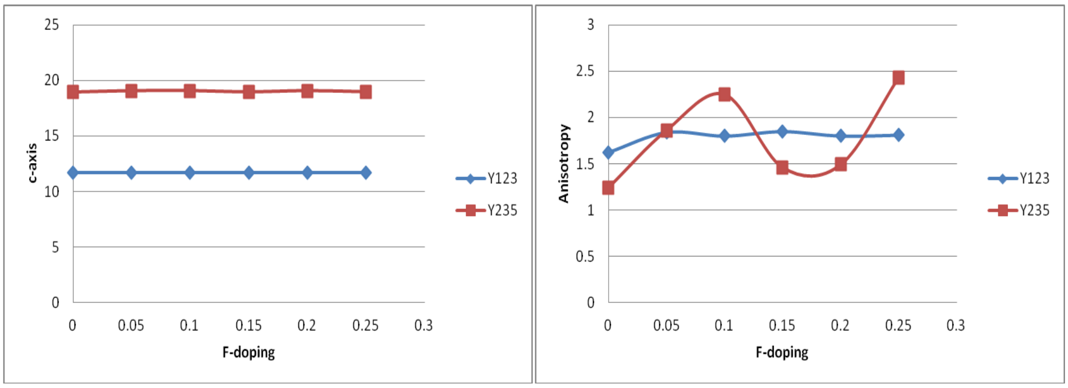

Fig. 3. The effect of F-doping on c-axis(a) on anistropy (b).

Iodometric titration analysis was used to determined oxygen content(O_y)[28] and the amount of $Cu^{2+}$and Cu^{3+} in $YBa_2Cu_3O_{7-x}$ and $Y_2Ba_3Cu_5O_{11-x}$.The Y123 and Y235 were high-temperature superconductors material contains both Cu^{2+} and Cu^{3+}[29-31] as a mixed-valence material[32]. The imbalance in charge is responsible for the oxygen vacancies in the lattice[33] and non-stoichiometric compounds in which the oxygen content was variable. The Y123 and Y235 have the coefficient(y) in the formula as non-integer value in the ranging from 6.5–7 for Y123 and 10.5-11 for Y235. The oxygen content (O_y) has been calculated by using the sum of the oxidation numbers of Y123 ($YBa_2Cu_3O_{7-x}$), and Y235 ($Y_2Ba_3Cu_5O_{11-x}$) were y = 7-x and 11-x, respectively. Here x is the deficiency[34] of samples. The Cu^{3+}/Cu^{2+} ratio, Oxygen content and the deficiency of all samples were shown in Table 2. For all samples of investigation found that the Y123 had the highest Cu^{3+}/Cu^{2+} percentage of deficiency and critical temperature.

Table 2.The oxygen content and deficiency of the samples.

compounds	Cu^{3+}/Cu^{2+}	Oxygen content(O_y)	Deficiency (%)
Y123	0.245	6.796	2.921
Y123+0.05F	0.236	6.736	3.764
Y123+0.1F	0.185	6.634	5.225
Y123+0.15F	0.280	6.678	4.594
Y123+0.20F	0.163	6.511	6.991
Y123+0.25F	0.117	6.407	8.467
Y235	0.189	10.602	3.619
Y235+0.05F	0.148	10.627	3.389
Y235+0.1F	0.154	10.567	3.935
Y235+0.15F	0.170	10.486	4.671
Y235+0.20F	0.117	10.538	4.202
Y235+0.25F	0.186	10.358	5.836

According to Fig.4. The Cu^{3+}/Cu^{2+} ratio versus the fluorine doping between of Y123 and Y235. The concentration of fluorine from 0 to 0.1, the Cu^{3+}/Cu^{2+} ratio were the closely value from 0.1 until 0.2, the bell shaped curve were found in both of Y123 and Y235. The concentration of fluorine had maximum at 0.15 of Cu^{3+}/C^{2+} value in Y123. The fluorine doped in Y235 occur the wielding the multiple values of Cu^{3+}/Cu^{2+}. Thus, the fluorine doped in Y123 was stable Cu^{3+}/Cu^{2+} value more than the Y235. In the many superconducting oxides, the addition is the essential factor in changing the electrical resistivity and structural properties[35-36]. Similary, The first cuprate superconductors of La214(La_2CuO_4)[37]was lost superconductor at ambient pressure. The charge of La, Cu and O were balance. Thus, La214 become superconducting doped Sr^{2+} cause addition electron/hole and the T_c increased as the number of holes. In 2004, H.C. Yu and K.Z.Fung[38] prepared La214 with doping Sr from x varied from 0 to 0.4 with the raw material of

La_2O_3, $SrCO_3$, and CuO by solid state reaction method. The maximum critical temperature at x=0.25 was found.

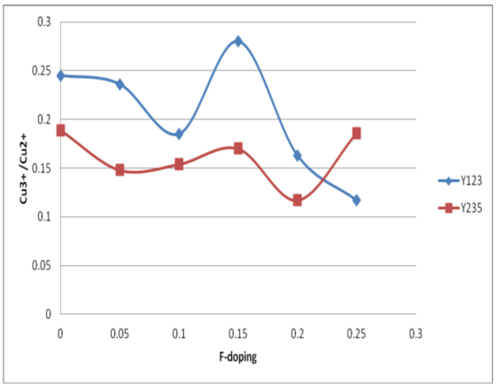

Fig. 4. The Cu^{3+}/Cu^{2+} *ratio versus the fluorine doping.*

In Fig.5. The blue and green curve was the oxygen content in Y123 and Y235, respectively. Both curves of the Y123 and Y235 were smooth lines. The more fluorine doping does not effective on the oxygen content in the both superconductors. Finally, the red and purple curve was the deficiency of Y123 and Y235. The pure Y123 was lowest deficiency value. For fluorine doped at 0 to 0.1, the deficiency value of Y123 was increasing.When 0.15, the deficiency drop obviously and then deficiency values increase again.This the point fluorine doping at 0.15, the two line of the both superconductors were overlap. The point is decrease of Y123 but increase of Y235. The different deficiency of pure and doped fluorine at 0.25 equal 5.55. However, the deficiency curve of Y123 was like a bell shape[39] but it overturned bell. For fluorine doped in Y235, the lowest deficiency value at 0.15, the maximum deficiency value at 0.25. Thus, different value of the lowest and maximum value of Y235 was 2.21. We can see that the deficiency value of Y123 had more the value than Y235 was about 2.5 times. Thus, the both superconductors, maximum value of fluorine will be the more deficiency value.

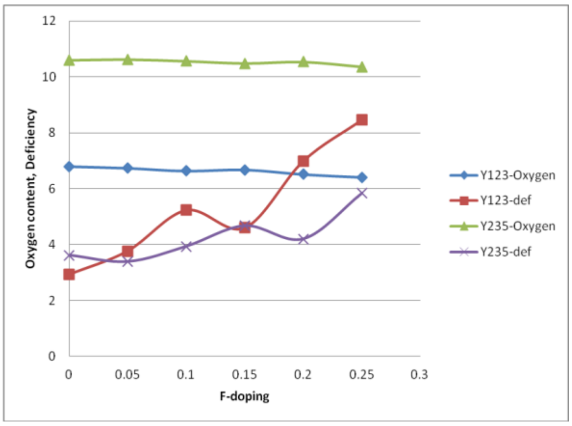

Fig. 5. Oxygen content and deficiency value versus Fluorine doping.

The effect of fluorine doping on the samples showed that there was a no effect of the *c*-axis on the both superconductors. The Y235 has difference of anisotropy more than Y123. However, Y123 has more different deficiency value than Y235. Because the anisotropy of YBaCuO material corresponds to an orthorhombic distortion and asymmetric distribution of oxygen. Additionally, these compounds have the structure with the layers of CuO_2 and Cu-O chains and complex structure. Therefore, the distortion of the structure of the material occur easily.

Then Y235 has Y atom more Y123,Y235 more orthorhombic distortion and asymmetric distribution of oxygen than the Y123.

Oxygen content and deficiency parameter used in this study created from Y123+F and Y235+F. The materials were ground, mixed and several heat treatment. Long annealing time was necessary to produce fully oxygenated sample. To prevent contamination has been taken to make sure all instruments used in the sample synthesis were cleaned thoroughly and crucial to repeatedly grind the sample homogeneity so that chemical reactions proceed in a uniform character[40].

4. Conclusions

The $YBa_2Cu_3O_yF_x$ ($Y123+F_x$) and $Y_2Ba_3Cu_5O_yF_x$ ($Y235+F_x$) with x = 0,0.05, 0.1, 0.15,0.2 and 0.25 synthesized by solid state reaction method with the calcinations temperature at 810 °C and sintered 925°C.The critical temperature onset of all samples were equal 92 K, 91 K, 95 K, 94 K, 94 K and 93 K, for $Y123+F_x$ and 92 K, 93 K, 93 K, 92 K, 92 K and 92 K for $Y235+F_x$ with x = 0,0.05, 0.1,0.15, 0.2 and 0.25, respectively. The Fluorine doping samples with x=0.1 was larger grain size and porosity reduction investigated by SEM.The resulted refine that grains and higher critical temperature.The compounds composition of the samples consist of two compounds fraction, the superconducting compounds (Pmmm) were orthorhombic structure and the non-superconductiong compounds was Y211(Y_2BaCuO_5) for Y123 and $BaCuO_2$(Im-3m) and $Ba_2Cu_3O_6$(Pccm) for Y235. The superconducting phase increase as the F-doping.The fluorine doping no effect in *a*,*b* and *c* axis value. The anisotropy parameter of Y235 was changing with the fluorine doping concentration increased more than Y123. The oxygen content, deficiency and Cu^{3+}/Cu^{2+} ratio of the samples characterized by iodometric titration method. The pure Y123 and Y235 were shown the highest of Cu^{3+}/Cu^{2+} ratio and deficiency parameter. The pure Y123 exhibits wasthe highest of oxygen content. The Cu^{3+}/Cu^{2+} ratio versus the fluorine doping shown the bell shaped curve are found in the both superconductors from 0.1 to 0.2. However, the quantity of doped materials has a limitation. At x = 0.2, the change on grain size and critical temperature have not found.Therefore, the amount of doped materials must be the appropriate quantity.

Acknowledgements

The author would like to thank the financial support of the Research and Development Institute of Suratthani Rajabhat University, Faculty of Science at Srinakharinwirot University and ThEP Center.

References

[1]T.Matsushitaet al.,Physica C. **201**, 151 (1992).
[2]A.Houghton et al., Phys.Rev.Lett.B.**40,**6763(1989).
[3]M.K. Wu et al., Phys. Rev. Lett.**58**, 908 (1987).
[4]D.N. Shiet al., Physica C. **270**, 274 (1996).
[5]P. Marsh et al., Nature.**334**, 660 (1988).
[6]P. Bordetet al.,Nature.**336**, 596 (1988).
[7]J. Karpinskiet al., Physica C. **161**, 618 (1989).
[8] J.Y. Genoudet al., Physica C.**192**, 137 (1992).
[9]A. Aliabadiet al., Physica C. **469**, 2012 (2009).
[10]www.superconductors.org, (A. Tavana acknowledges private correspondence with E.J. Eck).
[11]P. Udomsamuthirunet al., J Supercond Nov Magn.**23**, 1377 (2010).
[12]U. Topal and M. Akdogan, J Supercond Nov Magn. **24**, 1815 (2011).
[13]P. Chainoket al.,Advanced Materials Research.**770**, 295 (2013).
[14]J. H. Choyet al.,Bull. Korean Chem. Soc. **9**, 289 (1988).
[15]D. H. Ha et al.,J. Korean Phy. Soc.**39**, 1041 (2001).

[16]M.Mazaheriet al., J Supercond Nov Magn.**28,** 2637(2015).
[17]H.P. Roeseret al.,ActaAstronautica.**64**,391(2009).
[18]S.R. Ovshinskyet al., Phys.Rev. Lett.**58**,2579 (1987).
[19]S.R. Ovshinskyet al., Phys.Rev. Lett.**26**, 1189 (1987).
[20]K.Srinivasan et al., Journal of Minerals & Materials Characterization & Engineering. **10**,1277(2011).
[21]T.Kruaehong, Journal of The Australian Ceramic Society.**51(2)**, 109(2015).
[22]M. Merzet al.,Phys. Rev. Lett. **80**, 5192 (1998).
[23]J.M.T.Tranquadaet al.,Phys. Rev. B.**38**, 8893 (1998).
[24]R.J.Cava et al.,Physica C. **165**, 419 (1990).
[25]J.D.Jorgensenet al., Phys. Rev. B. **41**, 1863 (1990).
[26]S.Sujinnapramet al., Bull.Mater.Sci. **34**,1053(2011).
[27]T.Hamada and R.Morimo, Phys. Status Solidi A. **151**, 199(1995).
[28]A. Knizhniket al.,Supercond. Sci. Technol.**6**, 209(1993).
[29]P.K.Gallagheret al., Mat.Res.Bull.**22**,995(1987).
[30]M.Kikuchi et al., J.Appl.Phys.**26**, L1066(1987).
[31]Y.Saitoet al., J. Appl. Phys.**26**, L838(1987).
[32]J. G. Bednorz and K. A. Muller, Rev.Mod.Phys.**60**,585(1988).
[33]A. Punitha1 et al., Journal of Physical Science.**22(2)**, 33–49 (2011).
[34]D.Lederman et al., Appl.Phys.Lett.**64(5)**, 652(1994).
[35]C.Michel et al., Mater.Res.Bull.**20**,667(1987).
[36]A.N.Petrovet al, Solid State Ionics.**80**,189(1995).
[37]J.G.Bednorz and K.A. Muller, Z.Phys.,B.**64**,189(1986).
[38]H.C.Yu and K.Z.Fung., J.Mater.Res.**19(3)**,943(2004).
[39]F. Ishikawaet al., J.Phys.**150**, 052079 (2009).
[40]A.Bourdillonand N.X.TanBourdillon, High-Temperature Superconductors: Processing and Science, Academic Press, San Diego, CA 92101-4311(1994).