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CHARACTERIZATION OF Dy-DOPED AT Ca SITE IN LOW-DENSITY $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-X}Dy_XCu_3O_Y$ SUPERCONDUCTOR

(Pencirian Dy yang didopkan pada tapak Ca dalam ketumpatan rendah $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-X}Dy_XCu_3O_Y$ Superkonduktor)

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Abstract

Dysprosium-doped at Ca site in low density $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ with varying stoichiometry (where x=0.000, 0.025, 0.05, 0.1 and 0.2) were prepared by solid state method. In this work, the samples were characterized by X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), electrical resistance, and critical current density (J_C) measurements. All of the results indicated deterioration on the superconducting properties due to the substitution of dyprosium at Ca site compared to undoped samples. It has been observed that the J_C of low-density Bi-2223 at 60 K under zero magnetic field for Dy-free and x=0.050 (optimum doping level) was measured to be 12.120 A/cm^2 and 1.547 A/cm^2 respectively. Superconductivity transition temperature, T_C of undoped samples were found to be higher than doped samples. For undoped samples the $T_{C\ zero}$ was observed at 102 K and it decreased to 55 K, 66 K, 40 K and 40 K for x=0.025, 0.050, 0.100, and 0.200 respectively. The XRD results showed the c-axis decrease as the Dy doping increase and the crystal structure of the doping samples changed from tetragonal to orthorhombic. FESEM results showed the surface morphology of Dy doping indicated a weaker link between grains compared to the undoped samples.

Keywords: Superconductor, BSCCO, Dy-doped, Low-density

Abstrak

Dysprosium didopkan di tapak Ca kepadatan rendah $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ dengan stoikiometri yang berbeza-beza (di mana x = 0.000, 0.025, 0.05, 0.1 dan 0.2) telah disediakan melalui kaedah keadaan pepejal. Dalam kajian ini, sampel telah dicirikan melalui analisis pembelauan sinar-X (XRD), bidang pelepasan imbasan elektron mikroskop (FESEM), dan telah diukur rintangan elektrik dan ketumpatan arus kritikal (J_C). Semua keputusan penggantian Dyprosium di tapak Ca menunjukkan kemerosotan telah berlaku pada sifat-sifat superkonduktor berbanding dengan sampel yang tidak didopkan. Ia telah diperhatikan bahawa J_C ketumpatan rendah Bi-2223 pada suhu 60 K di bawah sifar medan magnet untuk sampel bebas Dy dan x = 0.050 (tahap optimum pendopian) masing-masing telah diukur dan mempunyai nilai 12.120 A/cm^2 dan 1.547 A/cm^2. Suhu peralihan kesuperkonduksian, T_C sampel yang tidak didopkan didapati lebih tinggi berbanding sampel yang didopkan. Untuk sampel yang tidak didopkan $T_{C\ sifar}$ diperhatikan berada pada 102 K dan ia menurun kepada 55 K, 66 K, 40 K dan 40 K untuk x = 0.025, 0.050, 0.100 dan 0.200. Keputusan XRD menunjukkan penurunan pada paksi-c disebabkan peningkatan Dy-yang didopkan dan struktur kristal sampel yang di dopkan juga berubah dari tetragonal kepada ortorombik. Keputusan FESEM menunjukkan permukaan morfologi Dy yang di dopkan lebih lemah pautan di antara butiran berbanding dengan sampel yang tidak didopkan.

Kata kunci: Superkonduktor, BSCCO,Dy-yang di dop, Kepadatan rendah

Introduction

The dopant process is drawing much attention and pertinent findings have been published especially regarding the understanding of the relevant parameters including the nature of charge carriers, structural stability, thermal stabilities, the effect of carrier concentration on the superconducting system, and others [1]. The improvement of superconductivity system is attributed to the increased density of mobile holes in CuO_2. However, sometimes the chemical doping method can cause the superconducting properties to become regressed. This is due to the decrement in the number of charge carriers (either holes or electron) in the material [2]. The substitutional studies of RE^{3+} at the Ca site in Bi-2212 superconductor revealed a repulsion between the CuO_2 layers, thereby increasing the CuO_2-CuO_2 plane separation. The increment of excess oxygen incorporated in between Bi_2O_2 double layers resulted in the increase in rare-earth concentration [3,4]. Some of substitution of rare earth elements can make the peak shift, hence indicates that the c-axis length decreases with the increment of substitution concentration. These variations of c-axis length show that the substituted RE enters into the crystal structure [5]. In this paper, we have characterized the Dy-doped at Ca site in low-density $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ superconductor via solid state method. The low-density samples have intermediate medium, known as porous structure. Interestingly, this structure has a high space factor that can operate at high current density [6]. In addition, the porous structure slightly improved the grain boundaries compared to high-density sample. And the strength of super current depends on the proportion of grain boundaries that are strong links [1].

Materials and Methods

Samples were prepared by applying solid state method. The high *Tc* superconducting samples with nominal composition of $Bi_{1.6}$ $Pb_{0.4}$ Sr_2 Ca_{2-x} Dy_x Cu_3 O_y (where x = 0.000, 0.025, 0.050, 0.100 and 0.200) ceramic superconductor were prepared from powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, Dy_2O_3, and CuO with 99.9% purity. The powders were weighed on a digital balance according to their stoichiometric ratio. The powders were milled together with an absolute ethanol in alumina pot for 24 hours. After milling processes, the homogenous mixture of powders was dried out in the oven at 120 ^{O}C for 6 hours. The powders were ground and pre-calcined at 800°C for 15 hours. Then the powder mixture was again calcined at 820°C for 15 hours to remove all oxides and carbonates. The powders were pressed to become a pellet of 2 grams by applying a pressure of 30 MPa. To form a high-density pellet, 2 grams of mixed powder was used. While 1.95 grams of mixed powder was added to 0.05 grams of polycrytalline sucrose to form a low-density pallet. The pellets were heated to 400°C for two hours to remove the sucrose. Finally, the resulting high-density and low-density pellets were sintered at 850°C for 72 hours to form a high T_C phase BSCCO superconductor. The samples (where x=0.000) were labelled as *A* for high density and *a* for low density. The substitution of low-density samples (where x=0.025, 0.050, 0.100 and 0.200) were labelled as *b*, *c*, *d* and *e* respectively. The high-density and low-density were obtained from high and low dimension and Archimedes water displacement technique using a densitometer. The samples were measured for their T_C, I_C, J_C using four point probe machine. X-ray diffraction (XRD) analysis of the product was carried out using Cu (K_α) radiation. The surface morphologies of the samples were studied using an FESEM machine.

Results and Discussion

Figure 1 shows the temperature dependence of electrical resistivity for undoped and doped samples with various Dy concentrations. All samples showed metallic behaviour up to the onset temperature (T_{on}), except for sample x=0.200 which showed semiconducting behaviour. For undoped samples, the $T_{C\ zero}$ was observed at 102 K and it decreased to 55 K, 66 K, 40 K and 40 K for x=0.025, 0.050, 0.100 and 0.200 respectively. At the point below and above the optimum concentration (x=0.050) of Dy where x=0.025 and x=0.100, the resistivity curve showed an inflection due to the double step transition and this means that Dy-doped at Ca site have weak links between the superconducting grains [7]. As a result, the substitution of Dy at Ca site were observed that the Dy^{3+} ion depressed the superconducting transition temperature.

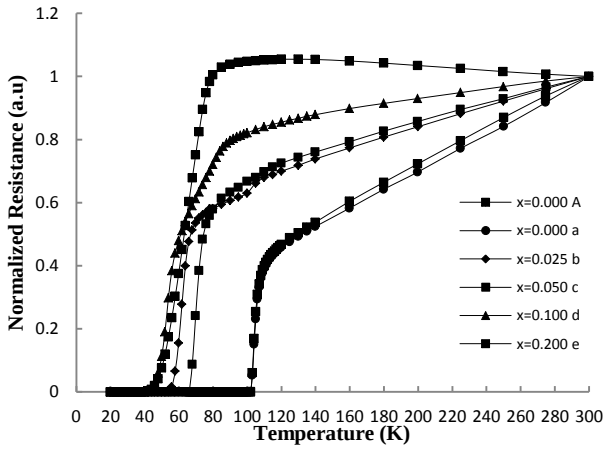

Figure 1. The temperature dependence of the normalized resistance

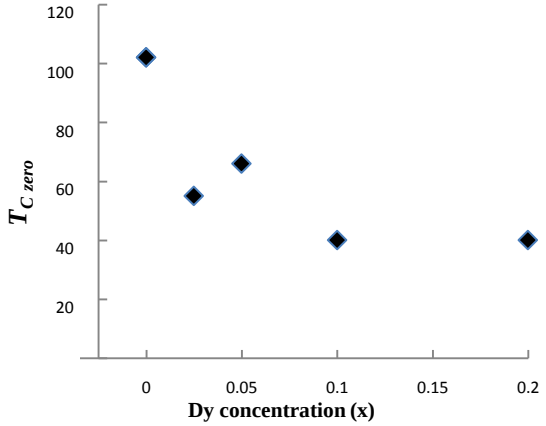

Figure 2. Variation of the carrier concentration with T_{Czero} (x=0-0.20)

The variation of the carrier concentration with $T_{C\ zero}$ (x=0-0.20) are given in Figure 2. The results obviously showed that the $T_{C\ zero}$ was more sensitive to the changes of Dy concentration. The doping samples exhibited increasing values of T_C towards the optimum concentration and decreased after increasing the Dy dopants further. The decreasing of $T_{C\ zero}$ values may be due to the weak link between BSCCO grains, distortions in the structure, and lattice defect of the dopant samples [8].

The Archimedes water displacement technique using a densitometer was used in order to measure the density of the samples. The obtained density from this technique showed that the density of high and low density of undoped samples were 6.00g/cm^3 and 4.67g/cm^3 respectively.

The critical current density, J_C of low-density undoped sample at 50 K and 60 K were found to be higher than the high-density undoped sample. This means that low-density undoped sample has a large current carrying capability compared to high-density undoped sample. This suggested that the porous structure has a high space factor and can operate at high current density [6].

Table 1. Critical temperature (T_C), critical current density (J_C), and hole concentration (P) for all samples

Sample code	Critical Temperature (K)			Critical current density J_C (A/cm^2)			Hole Concentration (P)	Bulk density (g/cm^3)
	$T_{C\,onset}$	$T_{C\,zero}$	ΔT_C	40 K	50 K	60 K		
A	109	102	7	14.471	12.075	10.567	0.1303	6.00
a	109	102	7	13.021	13.636	12.120	0.1303	4.67
b	65	55	10	2.717	1.4630	-	0.1168	5.11
c	85	66	19	2.998	2.418	1.547	0.1078	5.27
d	83	40	43	0.271	-	-	0.0808	5.14
e	80	40	40	0.185	-	-	0.0822	5.21

Sample 'A' represents high density

Table 1 shows the critical current density, J_C for undoped and doped samples with various Dy concentrations. All of the results showed that the deterioration on the superconducting properties was due to the substitution of dyprosium at Ca site as compared with the undoped samples. It has been observed that the J_C of low-density Bi-2223 at 60 K under zero magnetic field for Dy-free and x=0.050 (optimum doping level) were measured to be 12.120 A/cm^2 and 1.547 A/cm^2 respectively. The concentration value of Dy at x=0.050 was claimed as the optimum doping on the system due to the high critical current temperature, T_C and critical current density, J_C compared to other doped samples. At higher levels of substitution (x=0.200), the J_C values decreased. These were due to the increasing porosity, reduction of hole density, p and decreasing of inter-grain connectivity [5].

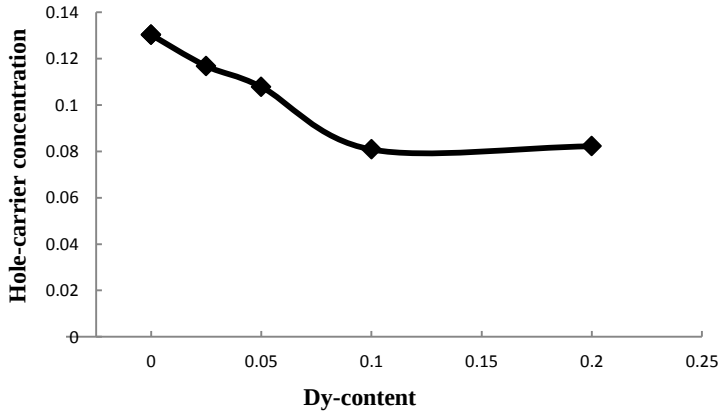

Figure 3. Variation of the hole-carrier concentration vs. Dy-content

The p-values of the samples have been calculated and are shown in Table 1. The variation of the hole-carrier concentration vs. Dy-content is also depicted in Figure 4. According to these results, the Dy substitution in low-density Bi-2223 system remarkably reduces the hole-carrier concentration and tends to decrease in the superconducting properties of the system. The destruction of the superconducting properties in BSCCO system extremely depends on the numbers of holein CuO_2 layers [8]. The substitution of Dy^{3+} ions at Ca^{2+} in this system reduce the number of effective holes, and usually increasing the oxygen content is not enough to compensate for the charge change. As a result, the number of holes in the CuO_2 planes decreased [9]. The density of mobile holes in the CuO_2 planes was associated with the high T_C superconductor and on the average Cu valence. The substitution of Dy^{3+} ions for Ca^{2+} ions leads to a decrement in the Cu valence [7].

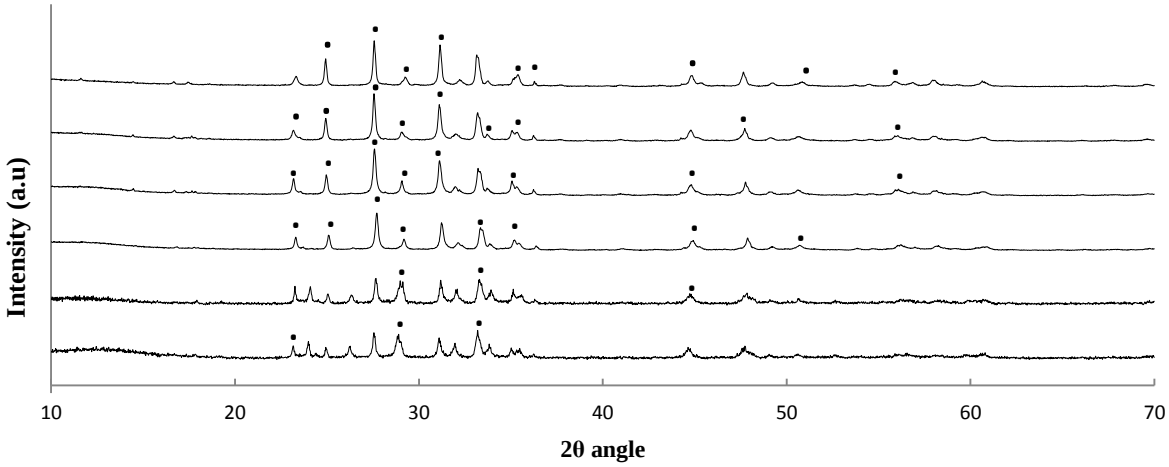

Figure 4. The X-ray diffraction pattern. The peak indexed represents Bi-2212

Table 2. Lattice parameter and relative volume fraction of the samples

Sample code	Dy Concentration	Lattice parameter (Å)			Volume ($Å^3$)	Volume fraction [%]	
		a	b	c		Bi-2223	Bi-2212
A	x=0.000	5.384	5.386	37.056	1074.558	83.76	16.24
a	x=0.000	5.384	5.386	37.076	1075.138	84.07	15.93
b	x=0.025	5.371	5.427	36.886	1075.168	51.61	48.39
c	x=0.050	5.371	5.429	36.970	1078.014	56.87	43.13
d	x=0.100	5.379	5.437	36.854	1077.818	31.12	68.88
e	x=0.200	5.388	5.455	36.812	1081.961	29.63	70.37

Sample 'A' represents high density

The results of XRD patterns of all samples are shown in Figure 4. As shown in Table 1, it can be seen that the lattice parameter of the crystal structure of high and low-density undoped samples is tetragonal whereby $a=b\neq c$. This means that the absence of organic peaks ($C_{12}H_{22}O_{11}$) proved that the sucrose addition to create open pores was completely burned out and did not affect the crystal structure [10].

However, as clearly seen from the lattice parameters, all samples of Dy-doped changed the crystal structure from tetragonal to orthorhombic whereby $a\neq b\neq c$. It is found that, the volume fraction 2223 decreased with the substitution of Dy^{3+} and vise versa for 2212 phase. This means that the intergranular contact decreased with higher ionic size of Dy^{3+} (1.05Å) substitute at Ca^{2+} (0.99Å) and led to the decreasing of Bi-2223 phase formation in this type of samples [11]. The results showed the length of c-axis decreased with the addition of Dy-doping. It is believed that the substitution of Dy into the Bi-2223 system distorted the bond structure and it changed the unit cell parameters [6].

The increasing of a-axis and b-axis as the results of substitution is very hard to understand. Since the length of both a-axis and b-axis were controlled by the length of the plane Cu-O bond. It is believed that the increment in a-axis and b-axis may result from the decrement of the hole concentration, which weakened the Cu-O bond [12]. This is correlated with the lowering of the transition temperatures and critical current density with the increment of Dy addition [7].

The enhancement of Dy content caused the broadening of the resistance increased. The results of the FESEM measurements support this phenomenon to happen due to the existence of weak links between the superconducting grains [2].

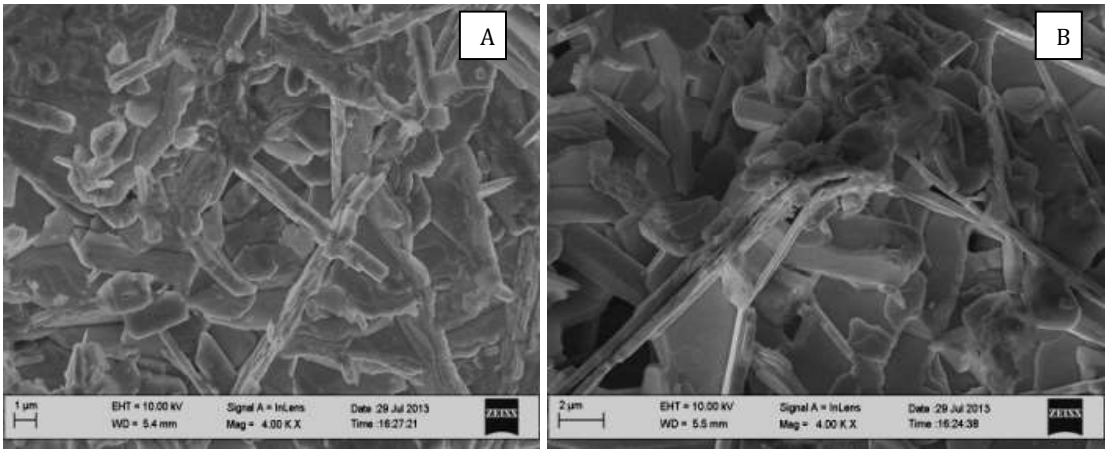

Figure 5. FESEM micrograph of the cross-section of the A) high-density and B) low-density undoped samples

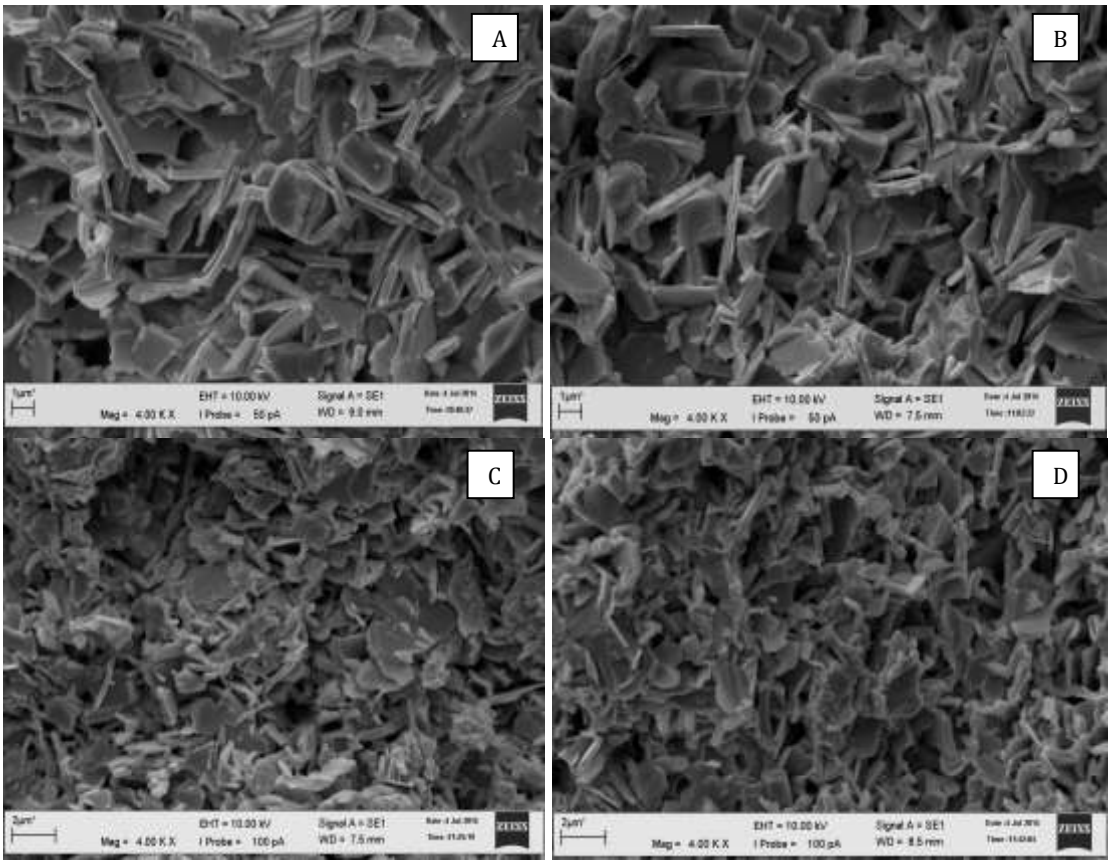

Figure 6. FESEM micrograph of the cross-section of the low density doped samples for A) x= 0.025; B) x= 0.050; C) x= 0.100; and D) x= 0.200

The FESEM images presented in Figure 5 show the morphology for the crystal of high and low density of the undoped samples. Plate-like particular structure is shown in sample *A*. There is a small amount of plate-like particulars, which are not crystallized and grain dimensions are not homogenous. The surface of sample *a* is larger with better grain boundaries. Furthermore, the grain morphology illustrates clear and flaky grains with layered growth.

Figure 6(a-d) represent the surface micrographs for the samples doped with Dy. Figure 6*a* and Figure 6*b* show the changing in grains compared to the low-density undoped-Dy sample. It was recognized that the oriented flake-like grains were obtained and some pores between the grains were observed. Figure 6*c* and Figure 6*d* show the granular formation on the surface that were obtained by increasing the Dy concentration, which have become smaller plate and randomly oriented shapes. It is suggested that the grain connectivity is worsened greatly with the increasing of Dy addition. This is related to the unstable behaviour of the Dy ions in the BSCCO system, because the Dy ions are more active than the Ca ions due to their small ionic radius [6].

Conclusion

The effects of Dy-doping on superconducting properties of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ crystal have been conducted. It was found that the substitution of Dy at Ca site indicated deterioration of the superconducting properties compared to the undoped samples. The doping samples exhibited increased values of T_C and J_C towards the optimum concentration and decreased after further increasing the Dy dopants. The destruction in the superconducting properties in BSCCO system extremely depends on the hole numbers in the CuO_2 layers [8]. The substitution of Dy^{3+} ions at Ca^{2+} in this system reduced the numbers of effective holes, and increased the oxygen content. The results showed that the length of c-axis decreased with the addition of Dy-doping. It is believed that the substitution of Dy into Bi-2223 system distorted the bond structure and changed the unit cell parameters [6]. FESEM results showed that the surface morphology changed with the addition of the Dy-atom in the low-density Bi-2223 and indicated a weaker link between grains compared to the undoped samples.

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References

1. Qureshi, A. H., Arshad, M., Durrani, S. K. and Waqas, H.(2008). Impact of Pb Substitution On The Formation of High T_C Superconducting Phase In Bscco System Derived Through Sol - Gel Process, *Journal of Thermal Analysis and Calorimetry* 94: 175–180.
2. Dogruer, S. B. M., Varilci, G. Y. A. and Zalaoglu, C. T. Y. (2012). Role of Cerium Addition on Structural and Superconducting Properties of Bi-2212 System, *Journal of Superconductivity and Novel Magnetism* 25: 847–856.
3. Pop, A. V., Ilonca, G., Ciurchea, D., Pop, V. and Deac, I. G.(2000). Effects of Y, Er and Lu substitution upon superconductivity in (Bi,Pb):2223 system, *Physica B : Condensed Matter* 284-288: 1101–1102.
4. Kaya, M. A. M. C., Ozcelik, B., Ozkurt, B. and Sotelo, A. (2013). Effect of Ce substitution on structural and superconducting properties of Bi-2212 system, *Journal of Materials Science: Materials Electronic* 24: 1580–1586.
5. Vinu,S., Sarun,P.M., Biju,A., Shabna,R. and Guruswamy,P. (2008). The effect of substitution of Eu on the critical current density and flux pinning properties of (Bi, Pb) -2212, *Superconductor Science and Technology* 21: 3–6.
6. Aksan, M. A., Altin, S., Balci, Y. and Yakinci, M. E. (2007). Structural characterization and transport properties of the HT_C $Bi_2Sr_2(Ca,Cd)$ $Cu_2O_{8+\delta}$ glass-ceramic rods, *Materials Chemistry Physics* 106: 428–436.
7. Terzioglu, C., Aydin, H., Ozturk, O., Bekiroglu, E. and Belenli, I. (2008). The influence of Gd addition on microstructure and transport properties of Bi-2223, *Physica B : Condensed Matter* 403: 3354–3359.
8. Ozkurt, B. (2013). Enhancement in superconducting transition temperature and J_C values in Na-doped $Bi_2Sr_2Ca_1Cu_{2-x}Na_xO_y$ superconductors, *Journal of Materials Science: Materials Electronic* 24: 2426–2431.
9. Jin, H. and Kotzler, J. (1999). Effect of La-doping on growth and superconductivity of Bi-2212 crystals, Physica C : Superconductivity, 325: 153–158.

10. Azhan, H., Fariesha F., Yusainee S.Y.S., Azman K. and Khalida S. (2013). Superconducting Properties of Ag and Sb Substitution on Low-Density $YBa_2Cu_3O\delta$ Superconductor, *Journal of Superconductivity and Novel Magnetism* 26(4): 931-935.
11. Sedky, A. (2008). On the influence of rare-earth substitution for Ca in Bi(Pb):2212 superconducting system, *Physica C: Superconductivity* 468: 1041–1046.
12. Lee, M. S. and Song, K. Y. (2002). Effect of Nd substitution for the Ca site in the 110 K phase of (Bi , Pb)–Sr–Ca–Cu–O superconductors, *Superconductor Science and Technology* 15: 851–854.