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EFFECT OF Zr ADDITION ON $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ SUPERCONDUCTOR

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ABSTRACT

The effect of Zr doping on 2223 phase of BSCCO system with general formula of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta Zr_X$ has been studied via XRD and resistance measurement to determine its crystalline structure and critical temperature, T_C respectively. All samples were prepared using conventional solid state reaction technique that involved a series of mixing and grinding. Generally, all samples exhibit metallic behaviour above $T_{C\ onset}$ (>108K except in x = 0.2 where $T_{C\ onset}$ ~ 80K). A single-step features was observed in all samples except in x = 0.15 and x = 0.2. The zero resistance temperature, $T_{C(R=0)}$ decreased as the content of Zr was increased with the Zr-free recorded the highest value at 100 K while the lowest $T_{C(R=0)}$ was recorded in x = 0.2 with 56 K. The ZrO_2 was incorporated into the crystalline structure of BSCCO system in all samples except for x = 0.15 and x = 0.2. A few peaks of ZrO_2 were detected in the samples. The volume for fraction of 2223:2212 in samples x =0.00 – x =0.10 is approximately 74:26 but drastically decreased to 38:72 in x = 0.15 and x = 0.20. The crystallographic structure remains in tetragonal form where a = b ≠ c. The c-lattice that plays an important role of superconducting properties was not significantly affected by the Zr addition up to x =0.10. However the c-lattice decreased in other samples.

Keywords: BSCCO; superconductor;

INTRODUCTION

Substitutions of various elements in BSCCO system were intensively studied by many researchers since the discovery of BSCCO system by Maeda et. al [1]. Most of the substitution enhanced the superconductivity at low concentration of dopants but caused detrimental effects if over-doped [2]. For example, partial substitution of Pb in Bi site of BSCCO has enhanced the formation of 2223 phase and therefore increased the onset temperature to 110 K [3]. However, V doped in Cu site of BSCCO has decreased the volume fraction of 2223 phase and shortens the c-parameter. These changes affected the T_C to decrease towards the V-doped. Some hypotheses were made such as destruction of phase coherence, loss of carries concentration and pair breaking effect [4]. Although the nano-ZrO_2 particles addition in BSCCO system suppressed the T_{Conset} gradually, the current density, J_C improved under magnetic fields due to the existence of artificial flux pinning created by excess ZrO_2 [5]. The study made by Zouaoui et. al on the nano-size ZrO_2 particles found that the morphology of the samples were not significantly affected

and therefore the J_C, activation energy of vortex flux and the volume pinning force density, F_P were improved [6]. In this paper, we have investigated the effect of ZrO_2 addition using ordinary chemical powder (99.9% purity) on the superconductivity of Pb-doped Bi-2223 superconductor.

EXPERIMENTAL PROCEDURE

The Zr-doped samples were prepared from Bi_2O_3, PbO, $SrCO_3$, CaO, ZrO_2 and CuO powders (each at least 99.9 % purity) in the correct stoichiometric amount to produce samples with compositions of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_30_\delta Zr_x$ using solid state reaction method. The concentration of Zr were in the range of x = 0.01, 0.02, 0.05, 0.1, 0.15 and 0.2. These powders were wet-milled with absolute ethanol in alumina pot for 24 hours and dried out in oven at 100 ^oC for 1 hour. Then the samples were calcined at 800 ^oC for 24 hours. Pre-sintering was done at 830 ^oC for 24 hours after grinding the powders using mortar and pestle. Finally, the powders of this nominal composition were pressed into disk shape with the diameter = 12 mm and the thickness = 2 mm before firing for 150 hours at 850 ^oC in a box furnace.

The x-ray powder diffraction patterns were checked using Cu-Kα radiation ranging from 10^o up to 70^o of 2θ-angle with an angular step of 0.02^o. The critical temperature, T_C was determined from electrical resistance measurements using the standard four-point probe technique fitted with a closed cycle helium cooling system, which is fully computerised. This system measures the voltage from 20 K to 300 K in a fixed current of 20 mA and the resistance was calculated by this system using ohm's law (V=IR). The field emission scanning electron microscope (FESEM) was used to identify the microstructure.

RESULTS AND DISCUSSION

The x-ray diffraction patterns for all pre-sintered samples (at 830 ^oC for 24 hours) are plotted in Figure 1. All samples consist of mixed phases such as 2212 and 2223. Almost 80% of 2212 phase detected in all samples and similar with the data reported by Pandey et. al [7]. Only one peak belongs to 2223 phase was detected at 17.76^o and labelled as H(002). The Zr peaks were detected in Zr-doped samples and highly dominated in x = 0.15 and x = 0.2. These results imply that the Zr is not yet incorporated into the crystal structure of BSCCO system. Pre-sintering process is not sufficient to form the 2223 phase, therefore sintering become an important process to form the 2223 phase. The purpose of pre-sintering process is to remove all carbonates and oxides from the samples and leaves $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_30_\delta Zr_x$ as a residual.

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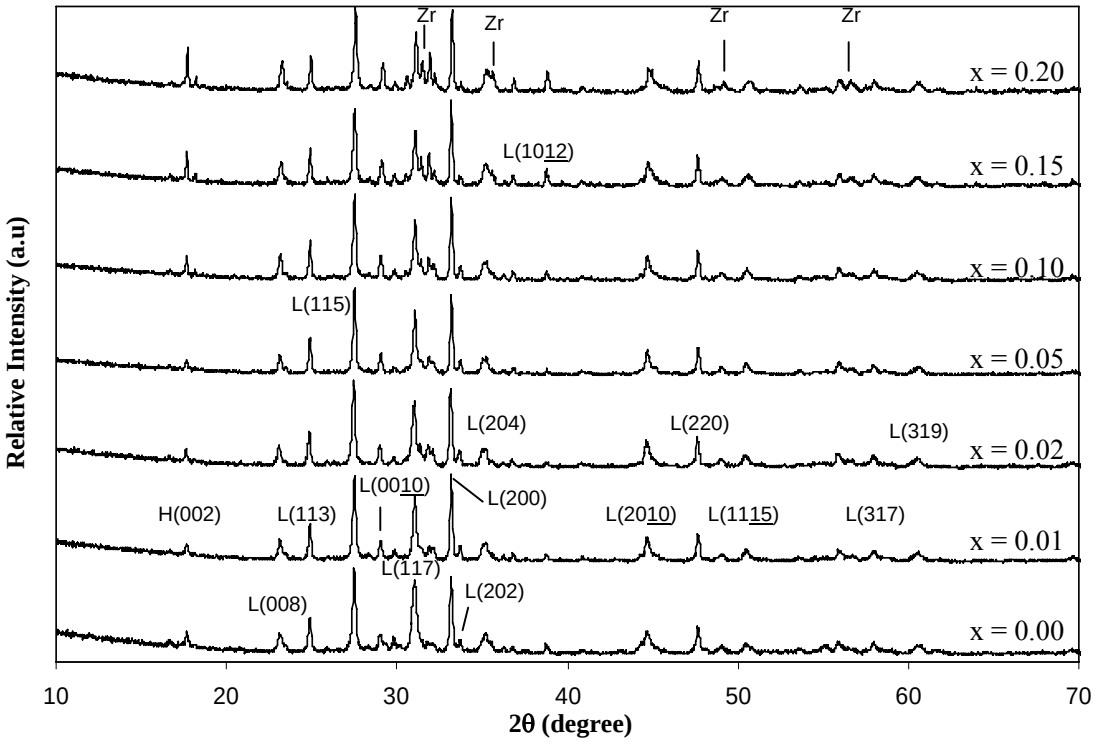

Figure 1: Pre-sintered at 830 ^{o}C for 24 hours. H – 2223 phase, L – 2212 phase

The X-ray diffraction patterns for all sintered samples at 850 ^{o}C for 150 hours are shown in Figure 2. The patterns depict mixed phases of 2212 and 2223. Zr peaks was not observed in x =0.00 until 0.10. However in x = 0.15 and 0.2, the Zr peaks was observed implying that the excess Zr is not incorporated into the crystal structure. Almost 70% of the peaks match with the data reported by pandey et. al [8] especially in Zr-free and other doped samples until x = 0.1. 60% of the peaks in x = 0.15 and x = 0.20 match with the data reported by Green et. al [9]. Table 1 summarized the calculated values of lattice parameter. All samples remains in tetragonal form. The length of c-parameter for Zr-free until x = 0.10 is almost the same but decreased in x = 0.15 and x = 0.20. The volume of unit cell in these samples also contracted to 885.0360 Å^3 and 883.8393 Å^3, respectively.

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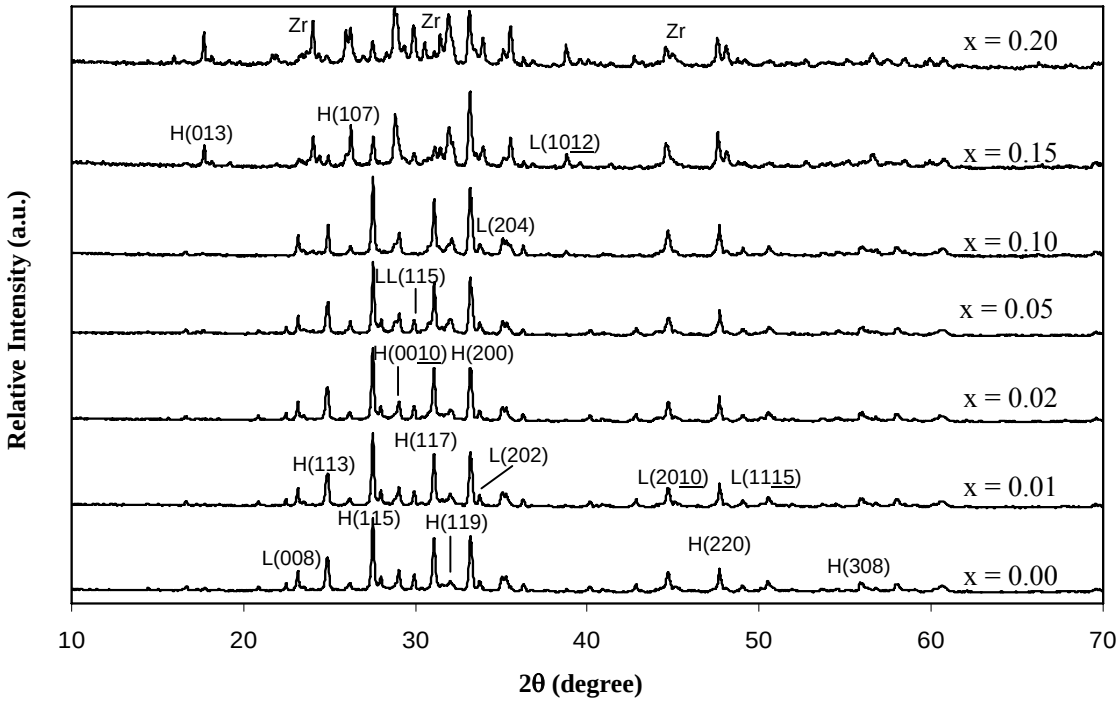

Figure 2: Sintered at 850 ^{O}C for 150 hours H – 2223 phase, L – 2212 phase

Table 1: Summarized of calculated values of lattice parameter for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta Zr_x$ samples

Zr Content (x)	**a (Å)**	**b (Å)**	**c (Å)**	**V (Å^3)**
0.00	5.3872	5.3872	30.666	889.97
0.01	5.3872	5.3872	30.666	889.97
0.02	5.3872	5.3872	30.666	889.97
0.05	5.3872	5.3872	30.666	889.97
0.10	5.3872	5.3872	30.666	889.97
0.15	5.3977	5.3977	30.377	885.03
0.20	5.4013	5.4013	30.295	883.83

Table 2: Volume fraction of 2223:2212 phase for sintered samples

Zr concentration (x)	Volume of fraction 2223:2212 (%)
0.00	73:27
0.01	74:26
0.02	74:26
0.05	73:27
0.10	76:24
0.15	38:62
0.20	38:62

The volume of phase ratio 2223:2212 as shown in Table 2 was calculated based on intensity of H(115), representing 2223 phase and intensity of L(00$\underline{1}$0), representing the 2212 phase. The ratio of these phases is almost similar in Zr-free until x = 0.10 but the ratio of 2223 phase decreased drastically to 38:62 in x = 0.15 and x = 0.20.

Figure 3 shows the resistance versus temperature for all sintered samples. Generally, all samples exhibit normal metallic behaviour above the onset temperature and therefore obey the Ohm's law (V=IR). The two-step features were clearly observed in sample with Zr concentration of 0.15 and 0.2. Both critical temperatures occurred at 110 K and 95 K for x = 0.15 and for x = 0.5 sample T_c appeared at 80 K and 66 K. Other samples exhibit a single-step feature with the onset temperature of ~108 K. When a virtual straight lines were plotted for these curves (beyond the T_{Conset} towards room temperature), the intercepts at y-axis made an inference to the level of doping i.e. the Zr-free sample has the highest purity and the lowest purity belongs to x = 0.2. The values of resistance as displayed by each curve were increased towards Zr concentration. The highest $T_{C(R=0)}$ was recorded at 100 K in Zr-free sample. In other samples, the values of $T_{C(R=0)}$ were gradually decreased until x = 0.15 and sharply dropped in x = 0.20. Table 3 shows the summarized values of critical temperatures for all samples.

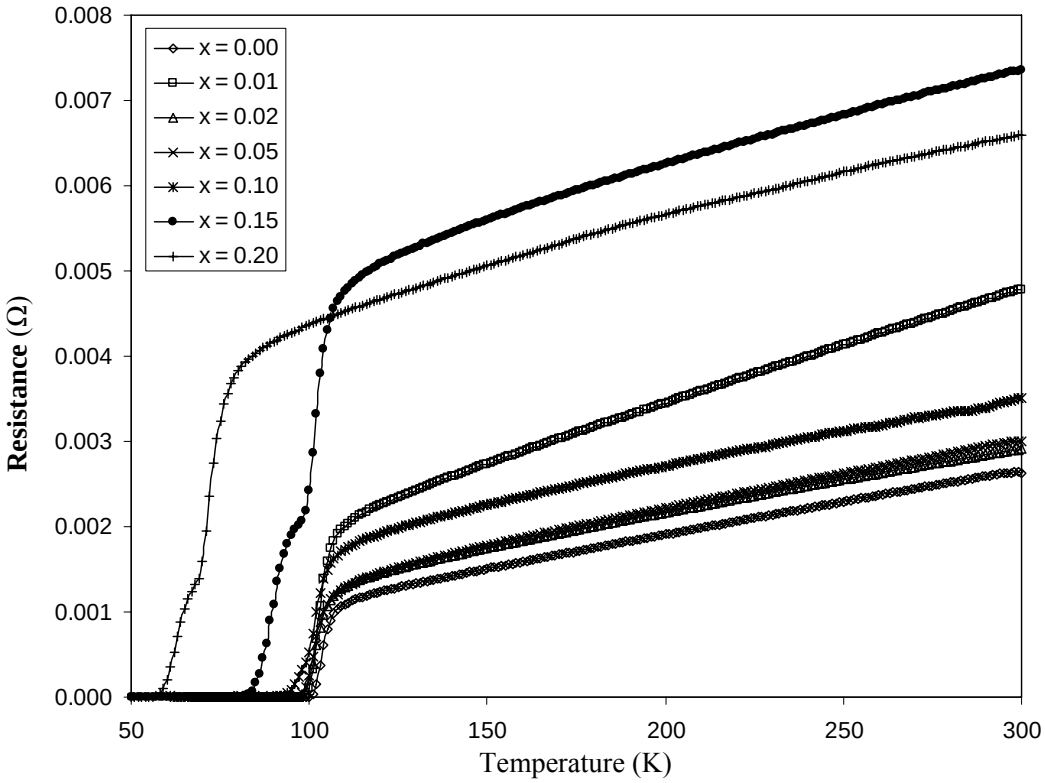

Figure 3: Resistance versus temperature for all sintered samples

Table 3: Summarized values of critical temperature, T_C for all samples

Concentration (x)	$T_{C(R=0)}$	1st T_{Con}	2nd T_{Con}
0.00	100	108	-
0.01	98	108	-
0.02	96	108	-
0.05	95	108	-
0.10	90	107	-
0.15	80	107	95
0.20	56	80	66

The T_C suppression towards Zr concentration in BSCCO system exhibits the strength of grains coupling decreased and therefore increased the weak-links [10]. Another factor that should be considered is a wave pairing function $\psi = \psi_O^{-i\phi}$ where the superconducting material can be destroyed by the reduction of amplitude (ψ_O) or by destroying the phase coherent (ϕ) [11, 12]. The pair breaking effect may contribute to sustain the T_C at approximately 110 K [13, 14]. The carriers coupling in Cu-O_2 plane also plays an important role in superconducting phenomenon of Bismuth-based superconductor. Substitution of impurities such as Zr in Copper atoms can change the superconducting properties and therefore altered the electronic structure of BSCCO system. It is possible that the spinning of impurity's electron such as Zr prevents the appearance of the superconducting correlation and thus decreased the zero temperature, $T_{C(R=0)}$ [4].

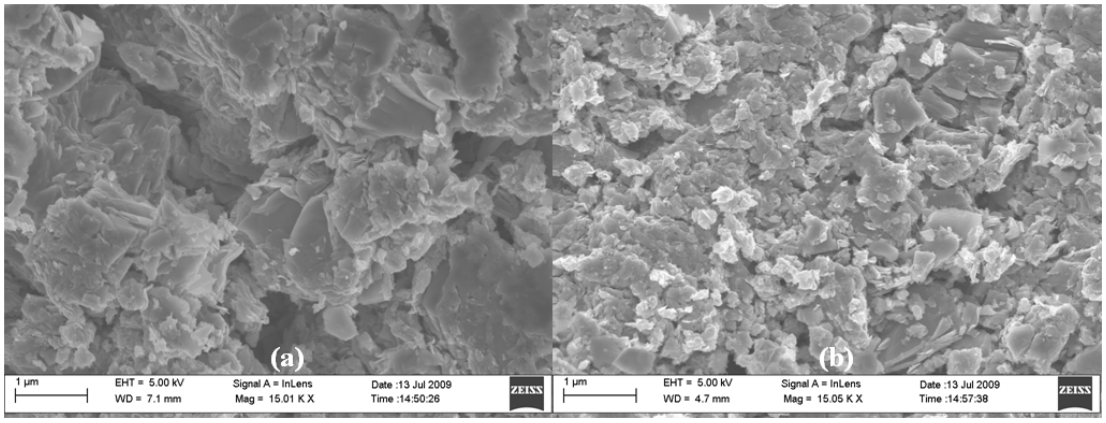

Figure 4: SEM micrographs of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta Zr_x$ samples sintered at 850 ^oC for 150 hours where (a) x = 0.00 (b) x = 0.01

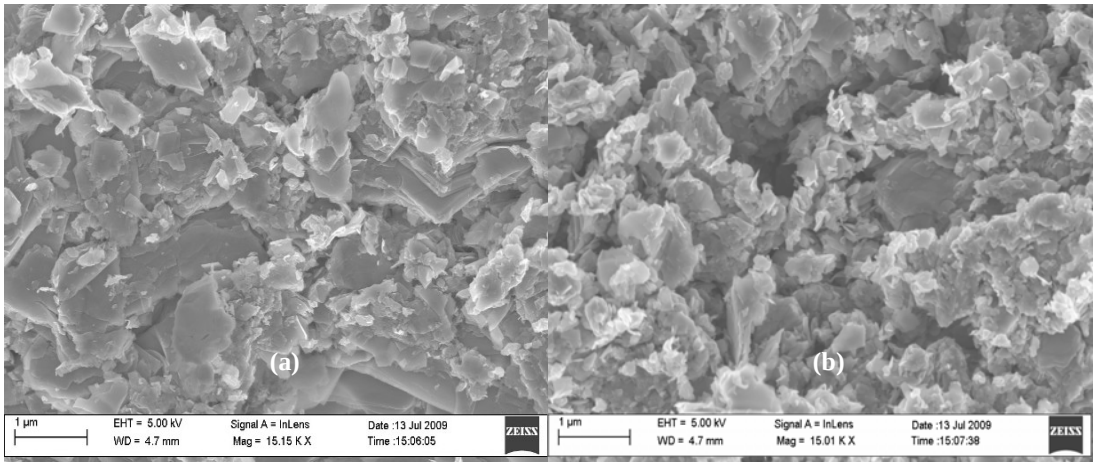

Figure 5: SEM micrographs of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta Zr_x$ samples sintered at 850 ^oC for 150 hours where (a) x = 0.02 (b) x = 0.05

SEM micrographs of fractured section for all samples are shown in Figure 4, 5 and 6. Generally, all samples displayed a thin flaky plate like grains with random distribution. The average length of grains in x = 0.00 – 0.1 is 1μm but in x = 0.15 and x = 0.20, the average length of grains increased to 7 μm. The content of voids decreases toward Zr concentration and therefore increases the sample's density. This feature can be seen clearly in sample x = 0.15 and x = 0.20.

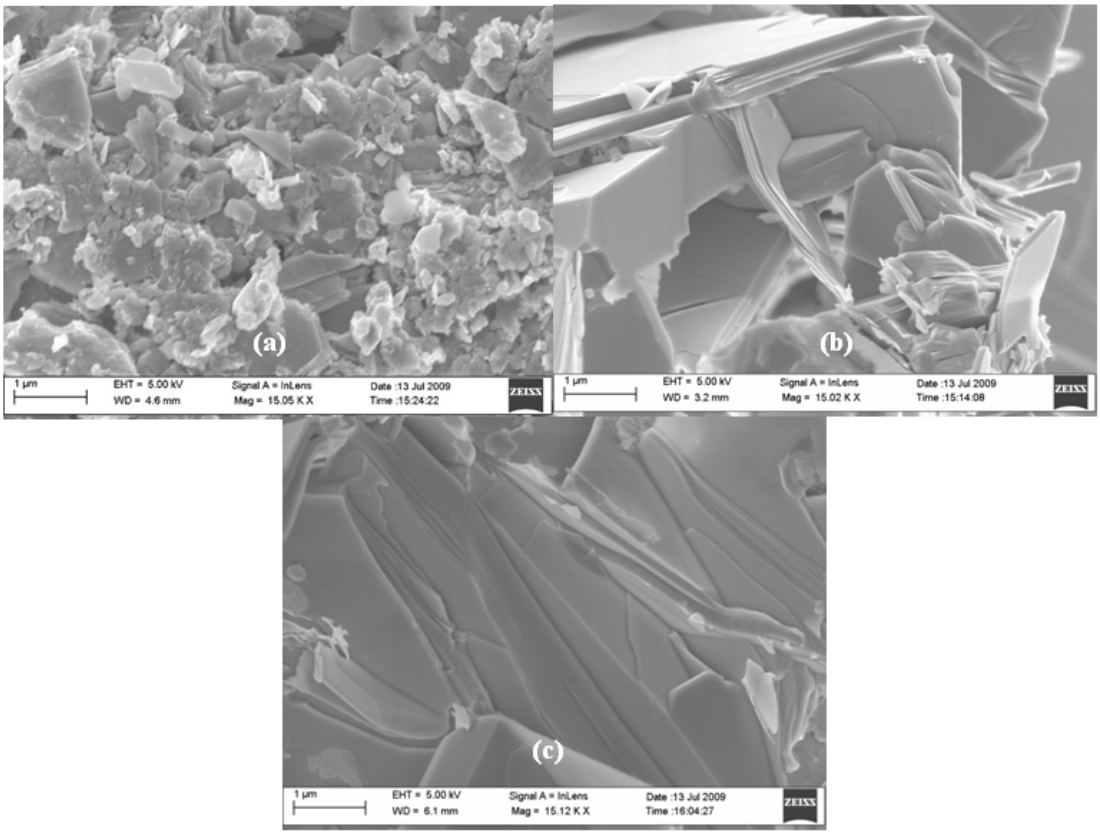

Figure 6: SEM micrographs of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta Zr_x$ samples sintered at 850 ^oC for 150 hours where (a) x = 0.10 (b) x = 0.15 (c) x = 0.20

CONCLUSION

The effect of Zr doping on 2223 phase of BSCCO system with general formula of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta Zr_x$ has been studied via XRD, resistance measurement and FESEM to determine its crystalline structure, critical temperature, T_C and morphology respectively. The ZrO_2 was incorporated into the crystalline structure of BSCCO system in all samples except in x = 0.15 and x = 0.2 samples. A few peaks of ZrO_2 were detected in both samples implying that it was not incorporated into the BSCCO crystal structure. The volume of phase ratio 2223:2212 is 74:26 in Zr-free until x = 0.10 but decreased to 38:62 in other samples. The crystallographic structure remains in the

tetragonal form where a = b ≠ c. The length of c-lattice that plays an important role of superconducting properties was not significantly affected by the Zr addition up to x = 0.10. However, the c-lattice was shortening in the last two. Generally, all samples exhibit metallic behaviour above the $T_{C\ onset}$. A single-step feature was observed in all samples except in x = 0.15 and x = 0.2 displayed two-step features. The value of zero resistance temperature, $T_{C(R=0)}$ decreased towards Zr concentration. A thin flaky plate-like grain with random distribution was observed in SEM micrograph. The average length of grains in x = 0.00 – 0.1 is ~1μm but in x = 0.15 and x = 0.20, it was increased to 7 μm.

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