Pertanika J. Sci. & Technol. **10(1)**: 135 - 143 (2002)

ISSN: 0128-7680

Studies of Sn Substitution on Ca and Cu Sites of Bi-Sr-Ca-Cu-O Superconducting System

H. Azhan[1], S. A. Halim[2], S. B. Mohamed[2], K. Azman[1], S. Y. S. Yusainee[1] & H. A. A. Sidek[2]

[1]Materials Science Research Group,
Universiti Teknologi MARA,
Kampus Jengka, 26400 Bandar Jengka,
Pahang Darul Makmur
[2]Superconductors and Thin Film Laboratory,
Physics Department,
Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia

Received: 16 November 2000

ABSTRAK

Kesan penggantian Sn pada tapak Ca dan Cu secara serentak atau berasingan dalam sistem Bi-Sr-Ca-Cu-O telah dikaji dengan menggunakan kaedah pembelauan sinar-x dan teknik pengukuran rintangan masing-masingnya untuk penentuan struktur dan suhu genting, T_C. Secara amnya, semua sampel menunjukkan sifat normal logam pada suhu melebihi suhu T_{Conset}. Nilai $T_{C(R=0)}$ didapati menurun terhadap kepekatan Sn. Walau bagaimanapun, nilai $T_{c(R=0)}$ untuk sampel x=0.02 yang didop dengan Sn secara serentak pada tapak Ca dan Cu diperolehi pada 104 K. Suhu ini meningkat sebanyak 4 K jika dibandingkan dengan suhu $T_{C(R=0)}$ sampel tulen. Sampel yang didop dengan Sn, untuk kepekatan x=0.20, pada tapak Ca atau kedua-dua tapak Ca dan Cu menunjukkan dominasi fasa-fasa 2212 dan 2201. Dengan yang demikian ubahsuaian terhadap persekitaran Ca membantu pembentukan fasa T_C rendah. Pemerhatian ini disokong oleh maklumat yang diperolehi melalui corak pembelauan sinar-x. Puncak-puncak baru yang tidak dikenal pasti (bendasing) dan puncak-puncak yang merujuk kepada fasa rendah 2201 muncul pada sampel dengan kepekatan Sn melebihi x=0.15. Tiada puncak yang dipunyai oleh SnO_2 dikesan dan ini bermaksud bahawa Sn mungkin telah bertapak ke dalam struktur kristal sistem BSCCO ataupun membentuk bendasing.

ABSTRACT

The influence of Sn substitution on Ca and Cu sites in Bi-Sr-Ca-Cu-O superconductor system simultaneously or separately have been studied using x-ray diffraction (XRD) method and resistance measurement technique for the structural identification and determination of critical temperature, T_C respectively. Generally, all samples displayed a normal metallic behavior above T_{Conset}. The values of $T_{C(R=0)}$ decreased towards Sn concentration. However, the $T_{C(R=0)}$ value for x=0.02 sample doped simultaneously in Ca and Cu sites was observed at 104 K. The critical temperature increased by 4 K compared to that of the pure sample. Sample doped with Sn, for concentration of x=0.20, at Ca site or at both Ca and Cu sites show the dominance of the 2212 and 2201 phases. Hence, altering the Ca environment favours the formation of the low T_C phases. This observation was also supported by the information obtained from the XRD patterns. New unidentified peaks (probably impurities) and low phase peaks corresponding to 2201 phase existed for samples with Sn concentration above x=0.15. No peaks belonging to SnO_2 were detected implying that Sn probably has been incorporated into the crystalline structures of the BSCCO system or formed as impurities.

Keywords: Superconductor, BSCCO, doping

INTRODUCTION

There are three stable phases in BSCCO system represented by a general formula, $Bi_2Sr_2Ca_{n-1}Cu_nO_y$. They were commonly referred to as 2201 phase (n=1, $T_C \sim 10$ K), 2212 phase (n=2, $T_C \sim 80$ K) and 2223 phase (n=3, $T_C \sim 110$ K) (Seshu Bai and Ravi 1991). Hence the formation of phases was due to the increasing content of Ca and Cu. In 2223 phase, partial substitution of lead in Bi-site was used to stabilize the formation of the phase and hence increased the volume fraction of 2223 phase and raised the T_C up to 110 K (Pisass *et al.* 1990). The effect of Ba doping at Ca site, both elements belonging to the same alkaline earth-group but having different ionic radii, in $Bi_2Pb_{0.6}Sr_2Ca_{2-x}Ba_xCu_3O_\delta$ suppressed the $T_{C(R=0)}$ but gradually decreased its value from 104K to 88K for x=0 to x=0.1 respectively (Halim *et al.* 1999). A partial substitution of V in Cu site, reduced superconducting properties in $(Bi,Pb)_2Sr_2Ca_2Cu_{3-x}V_xO_y$ by destroying the phase coherent (Nkum 1998).

It was believed that lead existed as Pb^{2+} and replaced Bi^{3+} in the structure and improves the superconducting properties for low concentration of lead substituted in Bi site of BSCCO superconducting system. At high concentration, lead also existed as Pb^{4+} and replaced other sites. The addition of Sn, which exists in two oxidation states, Sn^{2+} and Sn^{4+}, on Bi sites has reduced the volume of unit cell and reduced the formation of 2212 phase (Jha and Mendiratta 1996). Since tin have the similar electronic structure to that of lead, the study will be done to investigate the influence of a partial substitution of tin on Ca and Cu separately and both sites simultaneously on the superconducting properties.

EXPERIMENTAL PROCEDURE

The Sn-doped samples were prepared from Bi_2O_3, PbO, $SrCO_3$, CaO, SnO_2 and CuO powders (each at least 99.9 % purity) in the correct stoichiometric amount to produce samples base on these formula: $Bi_{1.6}Pb_{0.4}Sr_2(Ca_{1-x}Sn_x)Cu_3O_\delta$, $Bi_{1.6}Pb_{0.4}Sr_2Ca2(Cu_{1-x}Sn_x)_3O_\delta$ and $Bi_{1.6}Pb_{0.4}Sr_2(Ca_{2-x}Sn_x)_2(Cu_{1-x}Sn_x)_3O_\delta$. The concentration of Sn doping were in the range of x=0.02, 0.05, 0.10, 0.15, and 0.20. These powders were milled together with an absolute ethanol in alumina pot for 24 hours and dried out in oven at 120°C for 6 hours. These samples were calcined at 800°C for 24 hours. Further calcination was done at 830°C 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 = 1.2 cm and the thickness = 2 mm before firing for 150 hours at 850°C in a box furnace as a final sintering process.

The x-ray diffraction patterns were checked using Cu-Ka radiation in the range 2° up to 70° of 2θ angles with an angular step of 0.02°. The critical temperature, T_C was determined from electrical resistance measurements. The standard four-point probe technique was used for the electrical resistance measurement. The system fitted with a close cycle helium cooling system was fully computerised. Silver paint was used as electrical contacts between the samples and the probes.

RESULTS AND DISCUSSION

Normalised resistance at room temperature as a function of temperature for the samples doped with Sn in Ca site was showed in *Fig. 1.* All samples displayed a normal metallic behaviour above the T_{Conset} (transition temperature from metallic to superconductor). The $T_{C(R=0)}$ (zero resistance temperature) and T_{Conset} for the pure sample were obtained at 100 K and 110 K respectively. The widening of ΔT=10 K in this sample could be due to the existence of impurities. Formation of the low T_C phase favoured as the concentration of Sn increased from x=0.02 and x=0.05 as seen by the two-step features, thus reducing the $T_{C(R=0)}$. However, the two-step features were not observed for other concentration. The suppression of T_C values for the partial substitution of Sn in Ca site indicated that the strength of coupling between the grains of mixed phases has been decreased and hence, increased the weak-link (Nkum and Datars 1995).

The effect of Sn doping at Cu site on the temperature dependence of the resistance was displayed in *Fig. 2.* All samples, except sample with x=0.3, showed a normal metallic behaviour above the T_{Conset}. As observed for the curve belonging to x=0.02 sample, the resistive tail persists beyond $T_{C(R=0)}$ of the pure

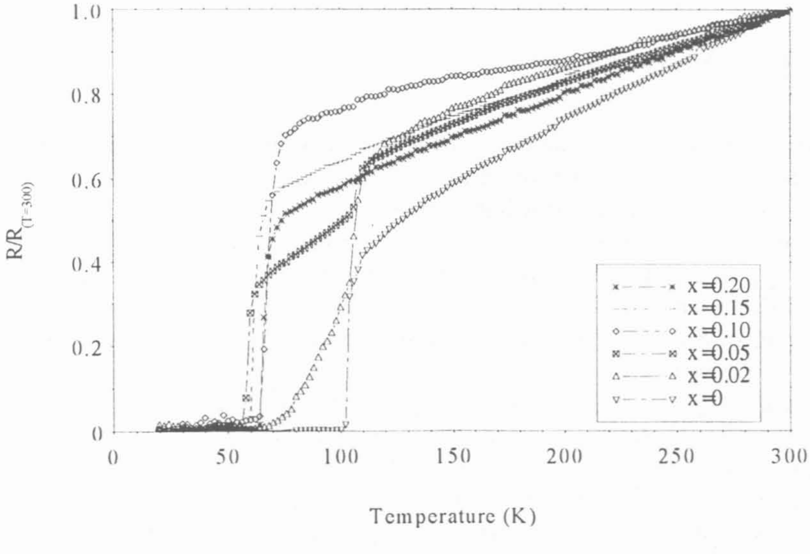

Fig. 1. Normalised resistance versus temperature for $Bi_{1.6}Pb_{0.4}Sr_2(Ca_{1-x}Sn_x)_2Cu_3O_\delta$

sample making ΔT very broad. This was due to the poor grain connectivity and the presence of low T_C phase. A two-step feature as clearly observed in all the samples except for the pure and sample with x=0.15. For samples with x=0.10 and x=0.15 the curves showed the improvement in $T_{C(R=0)}$ as compared to the samples doped in Ca site. It was a remarkable behaviour for the samples with x=0.20 and x=0.25 that showed a broadly improvement on the $T_{C(R=0)}$ and did not follow the trends of other samples that decreased the $T_{C(R=0)}$ with the increasing of Sn concentration. It was believed that the presence of resistive tail would be reduced after the heat treatment process implemented on these samples.

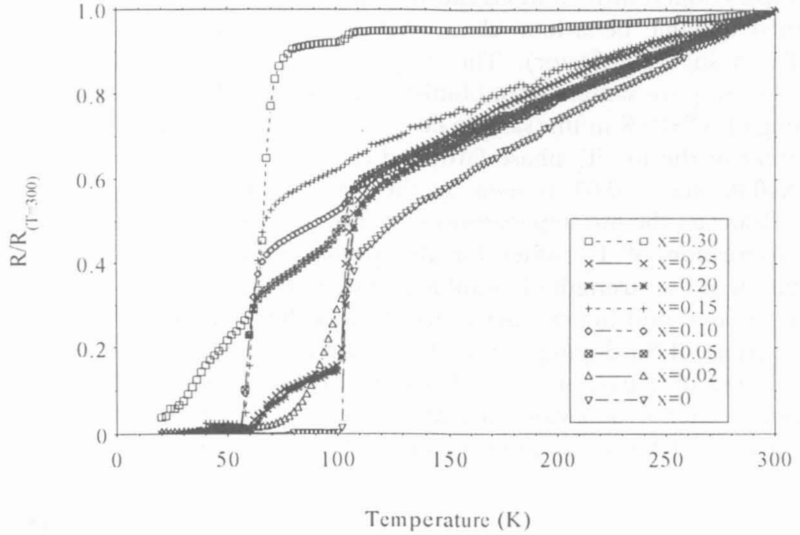

Fig. 2. Normalised resistance versus temperature for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{1-x}Sn_x)_3O_\delta$

The normalised resistance as a function of temperature for samples doped with Sn simultaneously at both sites of Ca and Cu was presented by *Fig. 3.* For this doping system, the doping concentration at x=0.02 was found to be favourable for the formation of 2223 high phase. Therefore increased the T_{Conset} and $T_{C(R=0)}$ as compared to that of the pure sample. However, other samples showed the normal trends, which decreased the T_{Conset} and $T_{C(R=0)}$ value with the increasing of Sn concentrations. A two-step transition was observed in samples with x=0.05, x=0.10 and x=0.15. Sample with x=0.20 does not achieve a zero resistance, $T_{C(R=0)}$ in the measured temperature range. The values of T_{Conset} and $T_{C(R=0)}$ for all samples were summarised in Table 1.

The x-ray diffraction pattern for all samples were plot in the range of 20°<2θ<40°. In the other range, the main peaks remain unchanged except for the pure sample, which showed the existing of 002 high phase peak. For doped samples, this peak disappeared. *Fig. 4* showed the x-ray diffraction pattern for

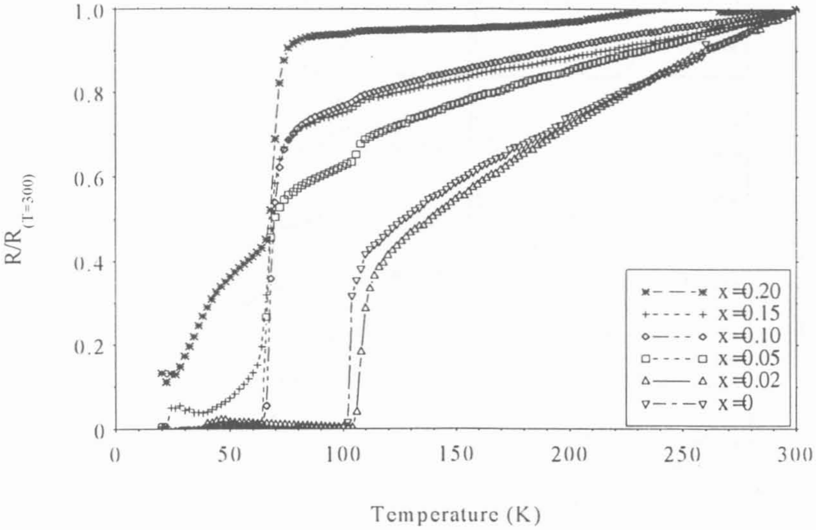

Fig. 3. Normalised resistance versus temperature for $Bi_{1.6}Pb_{0.4}Sr_2(Ca_{1-x}Sn_x)2(Cu_{1-x}Sn_x)_3O_\delta$

TABLE 1

T_{Conset} and $T_{C(R=0)}$ for all samples with a different concentration of Sn doped in Ca site, Cu site and both sites simultaneously

Sample Concen.	Sn doped in Ca site		Sn doped in Cu site		Sn doped in both sites	
	$T_{C(R=0)}$	T_{Conset}	$T_{C(R=0)}$	T_{Conset}	$T_{C(R=0)}$	T_{Conset}
0.00	100	110	100	110	100	110
0.02	60	112	66	114	104	114
0.05	56	110	54	110	64	110
0.10	64	76	56	108	64	80
0.15	58	70	54	108	58	70
0.20	62	72	54	110	-	78
0.25	-	-	58	112	-	-
0.30	-	-	23	106	-	-

the samples doped with Sn in Ca site. It can be observed clearly that 2223 high phase peaks dominated the pure sample. In Sn doped samples, some of the high peaks such as H(115) and H(00$\underline{10}$) disappeared. Some of the peaks in the Sn doped samples were shifted such as peaks H(00$\underline{12}$) as compared to that of the pure sample. One unidentified peak existed in the Sn doped samples and was marked as (*). This peak probably belongs to the impurity phase and it is believed that this peak correspond to the non-superconducting phase. The H(00$\underline{16}$) and LL(115) appeared in samples doped with x=0.15 and x=0.20. However, no peaks belongs to SnO_2 were detected implying that this oxide was incorporated into the crystalline structure (Nkum and Datars 1995; Melghit *et*

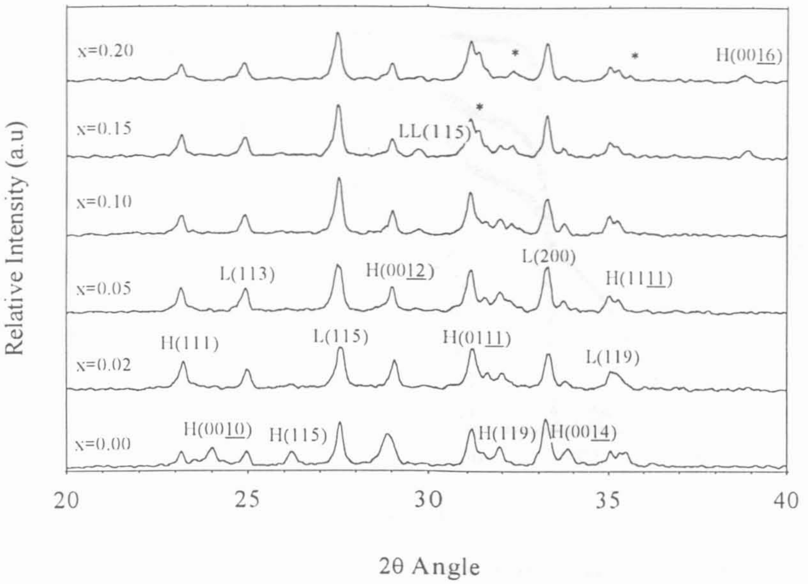

*Fig. 4. X-Ray diffraction patterns for $Bi_{1.6}Pb_{0.4}Sr_2(Ca_{1-x}Sn_x)_2Cu_3O_\delta$ (LL-2201 phase, L-2212 phase, H-2223 phase and *-unknown phase)*

al. 1998) or formed as impurities. The existence of unidentified peak and low phase peaks contributed to the lowered value of $T_{C(R=0)}$ and T_{Conset} as compared to the pure sample. These results almost synchronised with the T_C values obtained from resistance measurement technique.

Fig. 5 showed the pattern of x-ray diffractograph for the samples doped with Sn in Cu site. In this doping mode, some of the high phase peaks were not observed and was found to have almost a similar pattern with the samples doped with Sn in Ca site. The degree of phase shifting in the peaks of H(0012), H(0014), L(115) and L(200) were bigger than that of the samples in the Ca doping mode. About five unidentified peaks appeared in this doping mode. The decreasing of Cu concentration as well as the increasing of Sn concentration introduced new peaks and hence lowered the superconducting properties.

The x-ray diffraction pattern for the samples doped with Sn simultaneously in Ca and Cu sites was shown in *Fig. 6*. It is clearly observed that some of the peaks disappeared and shifted in Sn doped samples. A new peak correspond to 2201 phase appeared in x=0.20 sample and was identified as LL(113). The unknown peaks still existed in this doping system.

The information of XRD pattern obtained for the three doping systems showed that the influence of Sn might cause the loss of some high phase peaks and helps in the formation of low phase peaks. The increasing of the volume fraction of low phase peaks contributed to the lowering of T_C value. It also decreased the strength of the coupling between the grains and increased the weak links behaviour. The shifting of the peaks probably caused the shortening of c-parameter length. Since the length of c-parameter was known to be a very important criterion for the superconducting properties. The main reason for the shifting peaks was Sn that existed in two oxidation states as Sn^{2+} and Sn^{4+} replaced in all elements in BSCCO system and was incorporated into the crystalline structure. The ionic radii for Sn^{2+} and Sn^{4+} are 0.093 nm and 0.071 nm respectively. If there is no shifting on the peaks, the Sn^{2+} may only substitute onto Ca^{2+} (0.099 nm) and Sn^{4+} goes to Cu^{2+} (0.072 nm). It was believed that this happen at low concentration of Sn doping such as x=0.02 and x=0.05. However if the concentration of Sn increased, it will go to the other elements and modify the crystalline structure. All of the samples remained in a tetragonal form which $a=b\neq c$. The length of lattice parameters and the volume of unit cell were summarised in Table 2.

TABLE 2
The length of lattice parameter and the volume of unit cell for all samples

Doping System	Sn concen.	a(Å)	b(Å)	c(Å)	V(Å)^3
Sn doped in Ca site $Bi_{1.6}Pb_{0.4}Sr_2$ $(Ca_{1-x}Sn_x)_2Cu_3O_\delta$	0.00	5.3918	5.3921	37.837	1100.0
	0.02	5.3896	5.3897	37.836	1099.1
	0.05	5.3890	5.3887	37.830	1098.6
	0.10	5.3888	5.3883	37.826	1098.3
	0.15	5.3881	5.3879	37.824	1098.1
	0.20	5.3878	5.3870	37.820	1097.7
Sn doped in Cu site $Bi_{1.6}Pb_{0.4}Sr_2Ca_2$ $(Cu_{1-x}Sn_x)_3O_\delta$	0.00	5.3918	5.3921	37.837	1100.0
	0.02	5.3910	5.3904	37.818	1099.0
	0.05	5.3900	5.3895	37.775	1097.4
	0.10	5.3884	5.3881	37.710	1094.8
	0.15	5.3860	5.3865	37.506	1088.1
	0.20	5.3850	5.3853	37.490	1087.2
	0.25	5.3786	5.3780	37.175	1075.3
	0.30	5.3750	5.3764	37.114	1072.5
Sn doped simultaneously in Ca and Cu sites $Bi_{1.6}Pb_{0.4}Sr_2(Ca_{1-x}$ $Sn_x)_2(Cu_{1-x}Sn_x)_3O_\delta$	0.00	5.3918	5.3921	37.837	1100.0
	0.02	5.3914	5.3912	37.827	1099.5
	0.05	5.3894	5.3909	37.804	1098.4
	0.10	5.3891	5.3903	37.790	1097.8
	0.15	5.3878	5.3898	37.786	1097.3
	0.20	5.3866	5.3808	37.753	1094.3

CONCLUSION

Generally, all samples displayed a normal metallic behavior above T_{Conset}. The values of $T_{C(R=0)}$ decreased towards Sn concentration. However the $T_{C(R=0)}$ value for x=0.02 sample doped simultaneously in Ca and Cu sites is 104 K which increased by 4 K as compared to that of the pure sample. In other systems of Sn doping (doped in Ca site Cu site) the $T_{c(R=0)}$ decreased at this concentration.

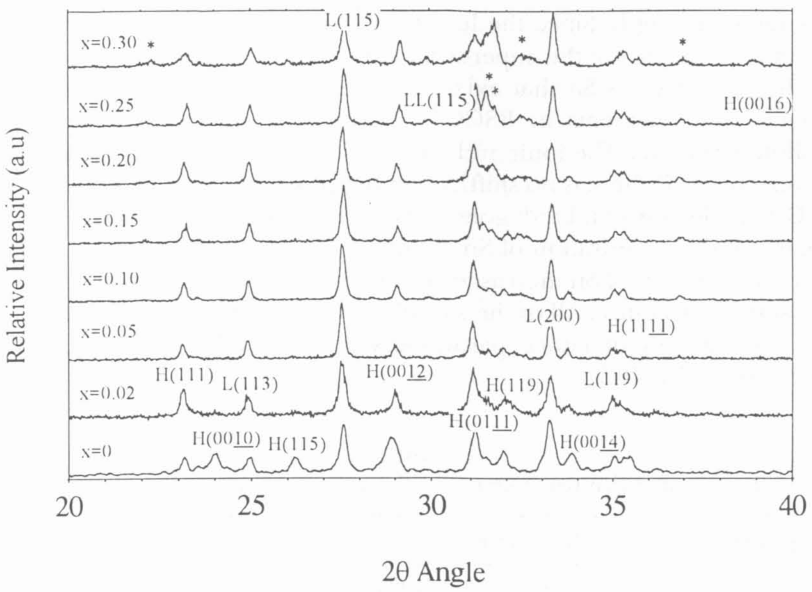

*Fig. 5. X-Ray diffraction patterns for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{1-x}Sn_x)_3O_\delta$ (LL-2201 phase, L-2212 phase, H-2223 phase and *-unknown phase)*

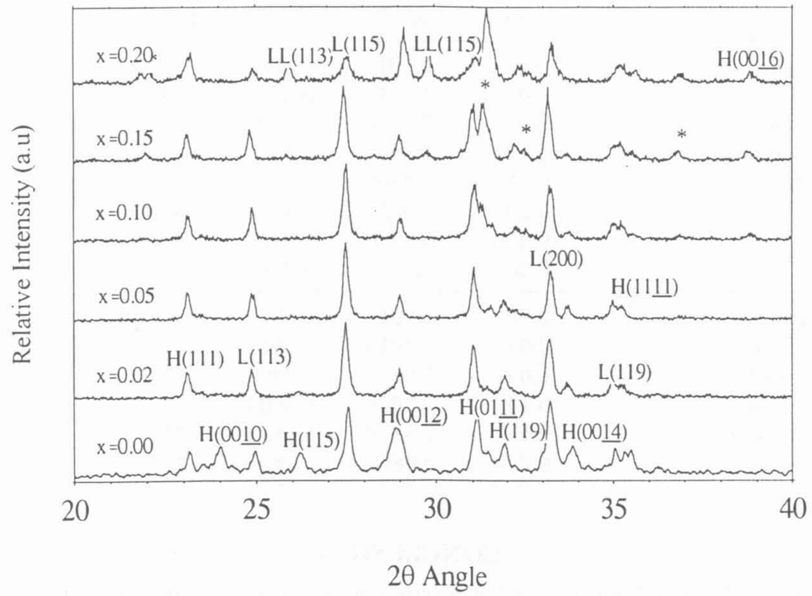

*Fig. 6. X-ray diffraction patterns for $Bi_{1.6}P_{b0.4}Sr_2(Ca_{1-x}Sn_x)_2(Cu_{1-x}Sn_x)_3O_\delta$ (LL-2201 phase, L-2212 phase, H-2223 phase and *-unknown phase)*

Samples doped with Sn in Cu site at x=0.20 and x=0.25 showed the lowering of resistive tail volume below the T_{Conset} as compared to the same value of Sn concentration in other doping systems. The decreasing of $T_{C(R=0)}$ and T_{Conset} with the increasing of Sn concentrations indicates that the substitution of Sn in BSCCO superconducting system did not favour for the formation of 2223 high phase but seems to be favourable to the formation of low phases (2212 and 2201). Sn as a non-magnetic element also reduced the coupling strength and hence increased the weaklinks between the grains. Some of the peaks have disappeared and shifted in the Sn doped samples. A new unidentified peaks and low phase peaks correspond to 2201 low phase exists at the level of Sn concentration above x=0.15. The existence of these particular peaks contributed to lower the superconducting properties in these systems.

ACKNOWLEDGEMENT

The financial support of the Ministry of Science, Technology and Environment Malaysia, under the Intensified Research in Priority Area (IRPA) vote: 4-07-05-026 (High Temperature Superconducting Materials and Device Applications) is gratefully acknowledged.

REFERENCES

NKUM. R. K. 1998. Superconductivity in $(Bi, Pb)_2Sr_2Ca_2Cu_{3-x}V_xO_y$. *J. Mater. Sci.* **33**: 207-210.

HALIM, S. A., S. B. MOHAMED, H. AZHAN, H. A. A. SIDEK and S. A. KHAWALDEH. 1999. Effect of barium doping in Bi-Pb-Sr-Ca-Cu-O ceramics superconductors. *Physica C* **312**: 78-84.

PISASS, M., D. NIARCHOS, C. CHRISTIDES and M. ANAGNOSTOU. 1990. The optimum percentage of Pb and the appropriate thermal procedure for the preparation of the 110 K $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ superconductor. *Supercond. Sci. Technol.* **3**: 128-133.

JHA, A. K. and R. G. MENDIRATTA. 1996. Effect of addition of barium, tin and silver on Bi-Sr-Ca-Cu-O ceramic superconductors. *J. Mater. Sci.* **31**: 1735-1740.

SESHU BAI, V. and S. RAVI. 1991. On the composition of 110 K superconductor in a (Bi, Pb)-Sr-Ca-Cu-O system. *J. Appl. Phys.* **70**: 4376-4382.

SANDEEP SINGH. 1998. Suppression of superconductivity in Sm and Co substituted $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$(system. *Physica C* **294**: 249-256.

NKUM, R. K. and W. R. DATARS. 1995. Weak links in ceramic In-doped Bi-Pb-Sr-Ca-Cu-O. *Supercond. Sci. Technol.* **8**: 822-826.

MELGHIT, K., S. RADHAKRISHNA and V. G. KUMAR DAS. 1998. *Trends in Materials Science*, ed. S. Radhakrishna, p. 181-193. New Delhi: Narosa Publishing House.