

THE EFFECT OF Pr SUBSTITUTIONAL DOPING IN 110 K PHASE OF (Bi-Pb)-Sr-Ca-Cu-O SUPERCONDUCTING CERAMICS

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ABSTRACT

The effect of Praseodymium (Pr) substitutional doping at varying concentration into the Strontium (Sr) site in the Bi-Sr-Ca-Cu-O (BSCCO) high temperature superconductor was investigated in this study. The samples were prepared via solid state reaction method. Its three properties; the electrical, the magnetic, and the structural properties of BSCCO superconducting system were measured according to the stoichiometric formula $(\text{Bi}_{1.6}\text{Pb}_{0.4})-(\text{Sr}_{1-x}\text{Pr}_x)_2-\text{Ca}_2-\text{Cu}_3-\text{O}_\delta$ where $x = 0.0 - 0.5$. Substitutional doping of Pr introduces impurities into the BSCCO compounds and this adds more holes as the oxidation state of Pr is 3+. In comparison for Sr, its oxidation state is 2+. The onset of critical temperature T_{Con} and zero resistance critical temperature $T_{\text{C(R=0)}}$ as x increases indicated the superconductivity destructive trend. Concurrently, its critical current density J_{C} also decreases. X-ray diffraction analysis were performed to determine the phase of the superconductor at varying concentration of doping level, to confirm that at starting composition $(\text{Bi}_{1.6}\text{Pb}_{0.4})$, the phases 2223 and 2212 (traces) co-exist at $T_{\text{Con}} \leq 110$ K.

INTRODUCTION

One of the important features of HTSC is the fact that these systems have one common theme; doping of elements into the parent compound. Doping in high temperature superconductors poses significant importance due to proximity of superconducting and insulating phases. Changes in the oxygen content, and its disposition and ordering can induce structural transformation, metal insulator transitions and variations in the T_{C} [1,2]

Substitution of rare-earth materials into a superconducting compound was generally expected to adversely affect the magnitude of $T_{\text{C (onset)}}$ and $T_{\text{C (0)}}$. However, Pr seemed to have puzzled the research community in this respect. Furthermore, the effects of Pr substitution in high-temperature oxide and cuprate superconductors have not been well understood. For example, the substitution of Pr for Gd in $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\square}$ (GdPr-

123) shows a lower T_C . This T_C reduction with increasing of Pr does not agree with Abrikosov-Gor'kov (AG) pair breaking theory [3]. When rare earth materials (which are very magnetic) were substituted into the Type II-YBCO system, superconductivity was not affected at all. But when Pr was added in, superconductivity was affected. Small amount of Pr was able to alter the transition temperature of YBCO system from 90 K to 0 K, depending on how much Pr was substituted for Yttrium. Pr is element 59 in the periodic table, from group III of non-radioactive metal element in Lanthanide series, a solid at 30 °C phases, and whose ions are magnetic. One possible explanation for this destructive effect to superconductor's critical transition temperature was a magnetic interaction between Pr and the superconductor compound, called hybridization [4].

Hybridization essentially depends on the extent of electron cloud around the Pr and O atoms in these complex systems. The ability of the rare earth elements to hybridize is greater for Pr than any other rare earth elements. So, Pr was able to have a type of magnetic interactions with these materials that eventually destroys superconductivity (ibid).

The objective of this study is to find out the effect of Pr substitutional doping of different concentration and heat treatment on the superconducting properties of BSCCO 2223 phase system.

EXPERIMENTAL DETAILS

Substitutional doping of Pr into the Sr-site with was performed by fabricating the ceramic samples using solid-state reaction method. The samples were prepared from Bi_2O_3 , PbO , SrCO_3 , CaO , Pr_2O_3 and CuO powders (all of at least 99.9% purity) in the selected stoichiometric amount to produce samples based on this formula $(\text{Bi}_{1.6}\text{Pb}_{0.4})-(\text{Sr}_x\text{Pr}_{1-x})_2-\text{Ca}_2-\text{Cu}_2-\text{O}_8$ where $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 . These powders were mixed and pulverized for 3 - 4 hours in an agate mortar and pestle until the powders became homogeneous. Next, the powders were calcinated at 800 °C for 24 hours. After pulverized, the homogenous powder was pre-sintered again at 830 °C for 24 hours. Then the powders were pressed into disc-shaped pellets and sintered in air at standard atmospheric pressure at 850 °C for 150 hours. Afterwards, the pellets were re-sintered at 855 °C for 30 hours. Measurement of the electrical properties (determination of T_C and j_C) was done on these pellets in a closed cycle helium cryostat, employing a four-point probe method. The structural properties of the samples such as lattice length and phase identification were determined using XPert PANAnalytical X-ray Diffractometer (XRD).

RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the curves of normalized resistance at room temperature ($T=300\text{K}$) versus temperature for sintered and re-sintered samples respectively. The general trend of the curves plot shows that as the level of doping increases, the T_C onset

and $T_{C(R=0)}$ were suppressed. The shapes of the curves for all samples displayed normal metallic behaviour above the onset of transition temperature, $T_{C(\text{onset})}$ and the gap between $T_{C(\text{onset})}$ and $T_{C(0)}$ is greater as x increases. Lowering of T_C indicated the presence of secondary Bi-2212 phase in the samples [5]. From earlier assumption, it was stated that Pr doping in the Sr-site increases the holes that act as the charge carriers [6]. A single-step feature can be seen clearly in sintered samples. In re-sintered, a two-step feature displayed clearly in $x = 0.3$ due to the existence of multiple low phases 2201 and 2212. Other samples exhibit single-step feature. The $T_{C(0)}$ in re-sintered treatment decreased beyond $x = 0.2$ as compared to that of the sintered samples. The $x = 0.5$ shows the worst when the $T_{C(0)}$ diminished. The suppression of T_C values also suggested that the strength of coupling between the grains of the mixed phases has been decreased, which in turn increased the weak link [7]. Table 1 summarized the critical temperature, T_C obtained from Fig. 1 and Fig. 2.

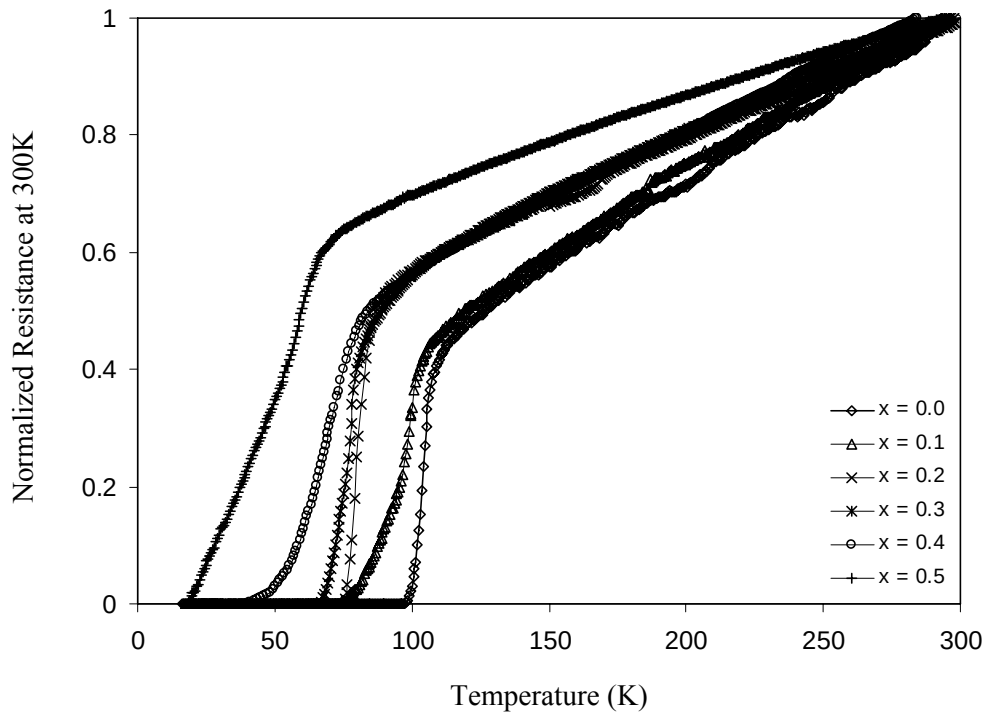


Fig. 1: Normalized resistance at 300 K versus temperature for sintered samples at 830 °C for 150 hours.

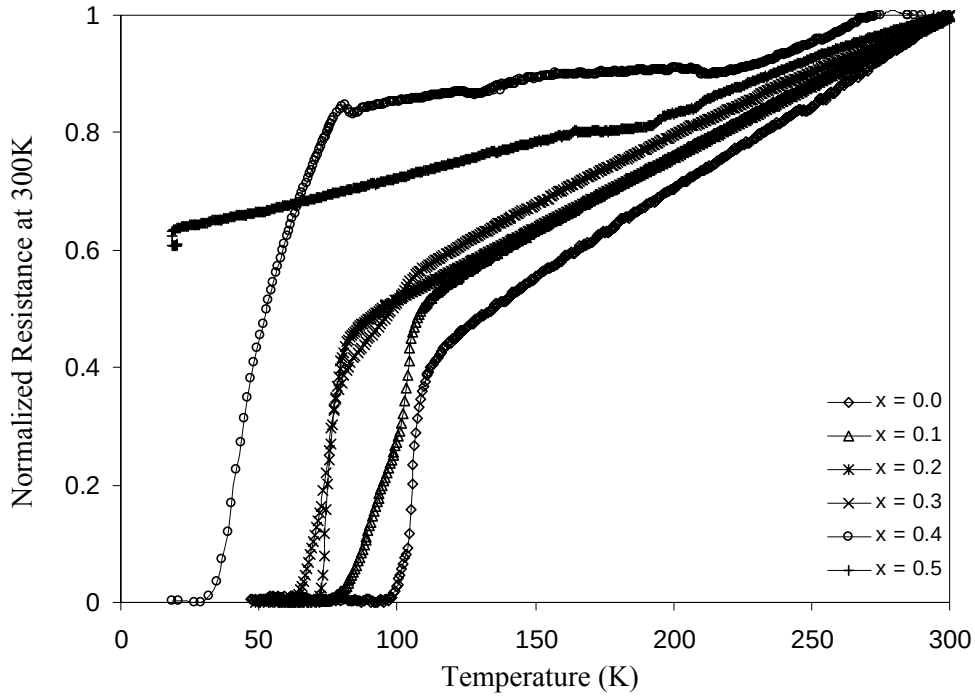


Fig. 2: Normalized resistance at 300 K versus temperature for re-sintered samples at 855 °C for 30 hours.

Table 1: Critical Temperature, T_C for sintered and re-sintered samples

Concentration of Pr, x	Sintered		Re-Sintered		
	1 st $T_{C \text{ onset}}$	$T_{C(0)}$	1 st $T_{C \text{ onset}}$	2 nd $T_{C \text{ onset}}$	$T_{C(0)}$
0.0	112	95	112	-	95
0.1	106	76	108	-	76
0.2	85	76	82	-	70
0.3	85	67	107	85	64
0.4	84	42	81	-	32
0.5	68	19	-	-	-

The highest value of critical current density, j_C was recorded in sample $x = 0.1$ i.e. 6934.04 mA mm⁻² in sintered and 14828.65 mA mm⁻² in re-sintered. Beyond $x = 0.1$, the j_C has decreased. For $x = 0.4$ and $x = 0.5$ of re-sintered samples, the j_C could not be recorded. From the summarized data of critical current density, j_C in Table 2, re-sintering process has improved the j_C of low doping ($x = 0.1$) of Pr which is also in good agreement with the T_C 's data and it seems to destroy the superconducting properties beyond that concentration.

Table 2: Highest critical current density j_c for sintered and re-sintered samples.

Doping Concentration, x	j_c (mA mm ⁻²)	
	Sintered	Re-sintered
0.0	4956.22	4905.30
0.1	6934.04	14828.65
0.2	4283.58	1839.08
0.3	506.42	1377.67
0.4	274.27	NA
0.5	203.29	NA

The XRD patterns for sintered and re-sintered samples were presented in Fig. 3 and Fig. 4 respectively. The patterns show that the evaluated crystalline lattice structure were mainly dominated by 2223 phase while 2212 phase exists as minority. The volume fraction of 2223 phase decreased while the volume fraction of 2212 increased towards the Pr concentration in both sintered and re-sintered. The length of c-axis decreased as doping concentration of Pr increased. This may be attributed to the precursor powders being incorporated into the lattice structure due to heat treatment. The crystallographic structures remains orthorhombic where $a \neq b \neq c$. The ionic radius of Pr^{3+} (1.01 Å) is smaller compared to Sr^{2+} (1.12 Å) [8] and therefore Pr^{3+} may goes into the Sr^{3+} site.

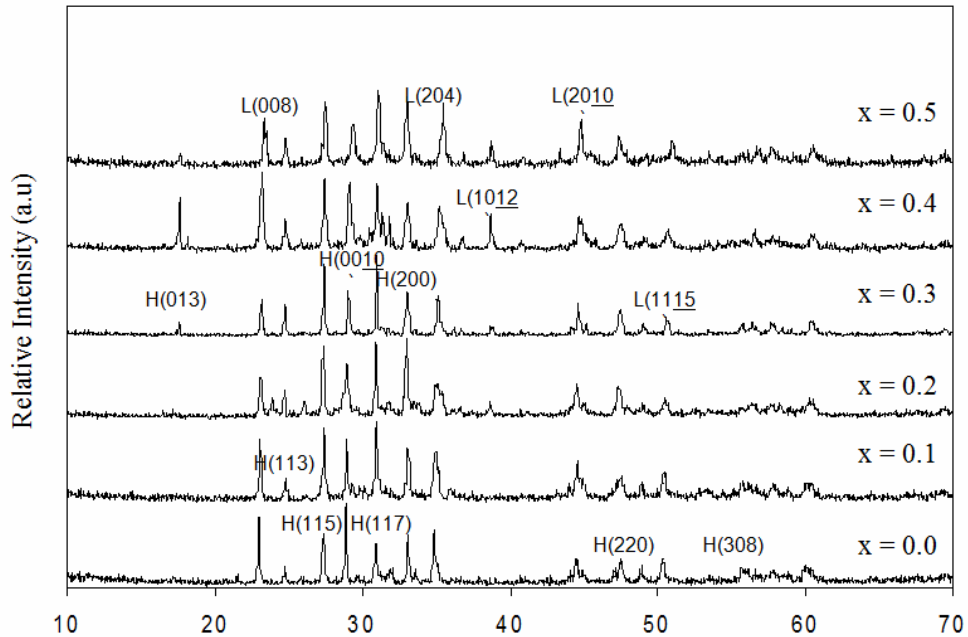


Fig. 3: XRD patterns for sintered samples where $x = 0 - 0.5$

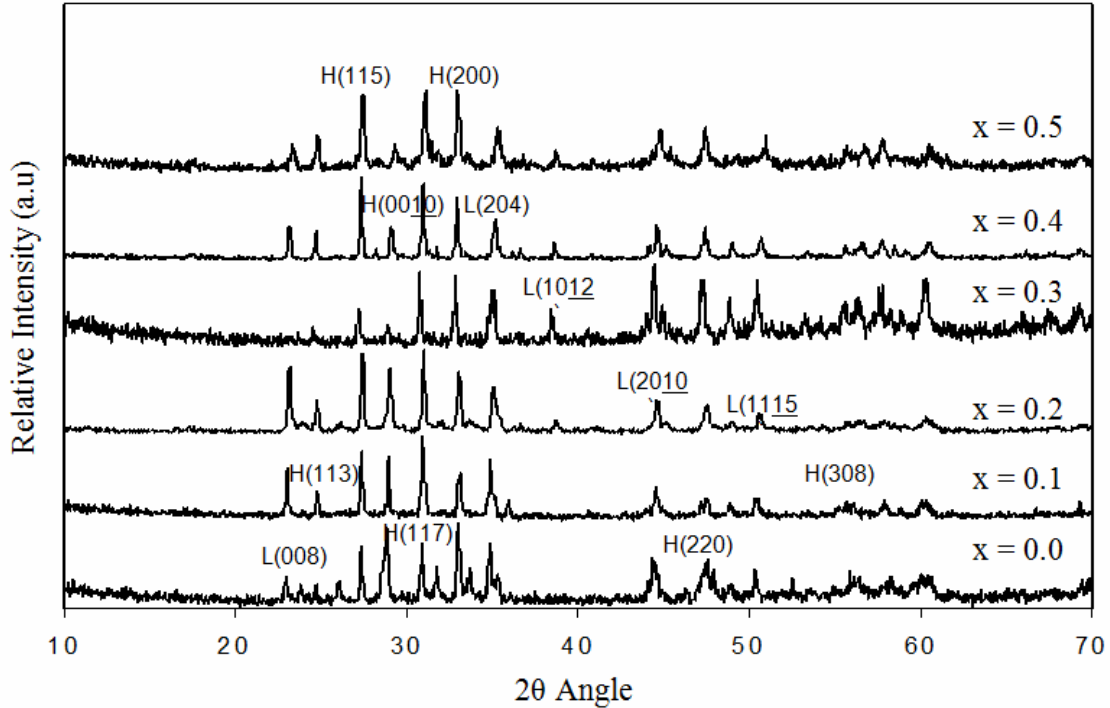


Fig. 4: XRD patterns for re-sintered samples where $x = 0 - 0.5$

At doping concentration of Pr in the Sr site of $x = 0.2$, optimal doping condition was obtained. Theories suggested that low levels of hole doping causes holes to become concentrated at certain locations resulting in hole-rich superconducting domains. Evidence suggested that rare earth cations Pr^{3+} situated at the Sr^{2+} site can decrease the T_C by decreasing the mobile carrier concentration through hole filling in the CuO_2 planes but optimised level is achieved when the Pr valence state is $3+$ [9]. Meng *et al* asserted that higher valence Pr will contribute more electrons to CuO_2 plane, filling the mobile holes responsible for conduction [10]. This was due to the effect of charge reservoir layer that lies adjacent to the CuO_2 layer that allows supercurrent to flow. According to Chu, the layered structure of cuprates HTSc can be represented by a generic formula $A_mE_2R_{n-1}\text{Cu}_n\text{O}_{2n+m+2}[A - m2(n-1)n-E]$ with a stacking sequence of m (AO) layers inserted between 2 (EO) layers on top of n CuO_2 layers interleaved by $(n-1)$ (R)-layers, where A, E and R are various cations [11]. Previous research was carried out on the Bi-2212 that has CuO_2 bilayer structure. This indicated that CuO_2 planes gives rise to superconductivity via the formation of Cooper pairs.

Table 3: Lattice parameters for sintered and re-sintered samples

Doping Concentration, x	Sintered at 850 °C for 150 hrs			Re-sintered at 855 °C for 30 hrs		
	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)
0.0	5.405	5.405	30.829	5.405	5.405	30.855
0.1	5.420	5.426	30.769	5.406	5.416	30.833
0.2	5.429	5.425	30.742	5.415	5.388	30.828
0.3	5.420	5.409	30.667	5.459	5.403	30.702
0.4	5.411	5.399	30.594	5.435	5.407	30.615
0.5	5.420	5.415	30.364	5.430	5.399	30.406

CONCLUSION

Doping with Pr increases the amount of ‘holes’ in the system at the CuO₂ layers, acting as charge carriers that reached optimum level at particular concentration $x = 0.2$, where transition temperature of the superconducting compound T_C increased slightly than the pure sample’s. Above this, as $x > 0.2$, T_C began to drop. This may be due to the higher valence of Pr above 3+ that contributes more electrons that fill the mobile holes in the CuO₂ planes. It is also observed that j_C decreased as the absolute temperature of the superconducting bulk samples increased. The maximum j_C occurred at $x = 0.2$. The hole filling effect is used to explain the effect of Pr doping in the Sr-site on the inconsistent behaviour of the superconducting material parameters, namely $T_{C(\text{onset})}$, $T_{C(\text{zero})}$, and critical current density j_C at higher temperature.

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