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A CLOSE CORRELATION BETWEEN DISORDERS-DEFECTS AND SUPERCONDUCTING TRANSITION TEMPERATURE OF $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ SUPERCONDUCTORS

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ABSTRACT

The enhancements of zero superconducting transition temperature ($T_{c,0}$) in $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ (BPSCCO) are reported. The BPSCCO samples (with x ranging from 0.00 to 0.06) were prepared by using the conventional solid state reaction technique. The properties of the samples were examined by using the X-ray diffraction (XRD), scanning electron microscopy (SEM), and the resistance versus temperature (R-T) measurements. From the XRD resuts, all samples revealed the orthorhombic structure, and the volume fraction of the Bi-2223 phase was varied as increasing x, and reached the maximum value of 82.72 % for x = 0.05 sample. Improvements of connectivity between the Bi-2223 grains in the Na-substituted BPSCCO samples were obtained by using the surface SEM images and a quantitive analysis of a correlation between $T_{c,0}$ and residual resistance ratio (RRR). A similar variation of $T_{c,0}$ of the samples as increasing x was observed. The highest $T_{c,0}$ enhancement of 107.5 K was obtained for x = 0.05 sample. Variations of the hole carrier concentrations in the CuO_2 layers were investigated, which also showed the highest value achieved for x = 0.05 sample.

Keywords: BPSCCO, Bi-2223, $T_{c,0}$, RRR

1. INTRODUCTION

In recent years, studies on applications of high temperature superconductors (HTS) have been received attention. Among the HTS materials, the Bi-Sr-Ca-Cu-O (BSCCO) system has been considered to be one of the most interesting superconductors due to its high superconducting transition temperature (T_c), and high critical current density (J_c) [1]. A nominal composition of BSCCO is expressed as $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$, where n is the number of CuO_2 layers corresponding to three superconducting phases, Bi-2201 (n = 1), Bi-2212 (n = 2) and Bi-2223 (n = 3) with T_c ~ 20, 80 and 110 K, respectively [2]. Therefore, Bi-2223 has been considered to be potential candidate for power-related applications of BSCCO superonducting wires and tapes. Numerous efforts have been devoted to the fabrications of BSCCO samples with high volume fraction of the Bi-2223 phase. It has been well known that a formation of the Bi-2223 phase is strongly depended on the sample fabrication conditions such as sintering temperature, sintering duration, precursor conditions, doped or substituted cations/anions. The first study on substitution effect has shown that the formation of the Bi-2223 phase was obviously improved by partially substituting Pb into Bi site [2-4]. Experimentally, it is relatively difficult to synthesize the Bi-2223 single phase because of the existence of the Bi-2212 (low T_c phase). The Bi-2223 phase was formed at high sintering temperatures which were close to its melting point (875 ^oC – 880 ^oC). By partially substituting Pb, the sintering temperature range was reduced, which revealed the enhanced formation of the Bi-2223 phase by means of a partial melting. Following these findings, the substitution effects using proper elements were carried out. Substitutions of alkaline metals such as Na, K, Li have been shown to positively affect the development of the Bi-2223 grains [5-7]. The hole carrier concentration has been found to play an important role on the superconducting properties, which provided clues on determining the characteristics of the BSCCO system. The hole carrier concentration in the consecutively stacked layers (CuO_2 planes) might be changed by either cationically substituting alkaline metals (valency of 1^+) into Ca/Sr/Cu (valency of 2^+) site or alterating the oxygen stoichiometry [5-7]. As a result, each substituting of the alkaline metals induced one hole, which led to the increase in the hole carrier concentration in the CuO_2 planes. Besides, dependences of zero critical temperature ($T_{c,0}$) on the sample quality have been studied by using the residual resistance ratio (RRR) – which was closely related to the lattice structural disorder [8]. Motivated by these developments, effect of Na-substitutions on the structural and superconducting properties of BPSCCO samples was investigated. Enhancements of $T_{c,0}$, increases in the hole carrier concentration and linear dependence of $T_{c,0}$ on RRR were found in our $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples.

1. MATERIALS AND METHODS

The polycrystalline $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples with Na concentration ranged between x = 0.00 to 0.06 were prepared by using the conventional solid state reaction technique. The appropriate weights of starting materials of Bi_2O_3, PbO, $SrCO_3$,$CaCO_3$, CuO and Na_2CO_3 , all of 99.99% purity, were taken with precise values. The powders were thoroughly mixed and ground using agate mortar with a solvent of C_2H_5OH (99.5%) in order to homogenize the mixture and to get fine powders. The mixed powders were then pelleted and undergone the 4 calcination stages from 670 to 820 $^\circ$C. Each stage was last for 48 hours in air with the re-grinding and re-pelleting steps. The sintering process was performed at 850 $^\circ$C for 168 hours in air, then the samples were freely cooled to room temperature.

X-ray diffraction measurement was used to determine crystal structure and fractions of high and low T_c phases. The scanning electron microscopy (SEM) was conducted to examine the surface morphology and grain distributions. The resistance measurement was performed by using the standard four-probe method in the He closed-cycle cryostat system to investigate the superconducting property as well as superconducting transition temperature of the samples.

2. RESULTS AND DISCUSSION

The XRD patterns of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples are presented in Figure 1. The 2θ angle was scanned from 10º to 70º in order to detect all XRD peaks. It could be seen that all fabricated samples are polycrystalline and their structures are orthorhombic. Also, all fabricated samples were mainly consisting of low T_c (Bi-2212) and high T_c (Bi-2223) phases denoted by L and H, respectively. The only non-superconducting phase was found in all samples was Ca_2PbO_4 and marked by "+" [6-7]. The appearance of Ca_2PbO_4 phase was attributed to the chemical reaction of Pb with Ca during the calcination process, which played a key factor in enhancing the formation of the Bi-2223 phase [2,5-7]. More than two phases existed in the samples might be related to formation of stacking faults perpendicular to the c-axis [7]. To quantitively compare changes in the formation of the superconducting phases, the volume fraction of each phase was estimated by using the following relation [8]:

$$\%\mathrm{Bi}-2223=\frac{\sum I_{2223}}{\sum I_{2223}+\sum I_{2212}}\times 100 \quad (1)$$

$$\%\mathrm{Bi}-2212=\frac{\sum I_{2212}}{\sum I_{2223}+\sum I_{2212}}\times 100 \quad (2)$$

where I2223 and I2212 were the intensities of the XRD peaks for the Bi-2223 and Bi-2212, respectively.

Table. 1. Volume fractions of the Bi-2223, Bi-2212 phase and average size of the Bi-2223 grains

Na (x)	% Bi-2212	% Bi-2223	d (μm)
0.00	25.77	74.23	9.6 ± 0.12
0.01	21.31	78.69	10.1 ± 0.10
0.02	20.83	79.17	10.2 ± 0.13
0.05	17.28	82.72	10.7 ± 0.14
0.06	18.82	81.18	10.6 ± 0.12

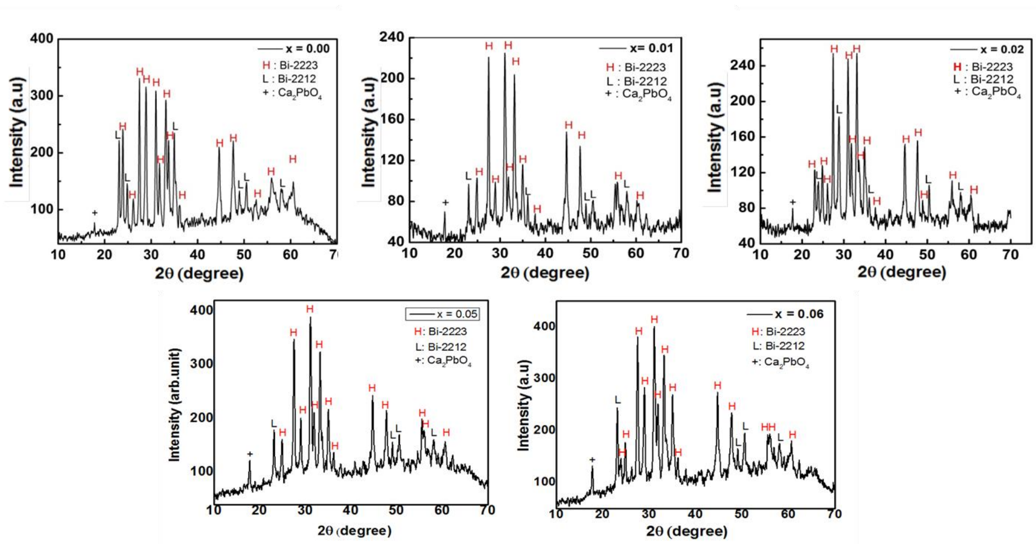

Figure 1. Xray diffraction patterns of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples

The estimated values are listed in Table. 1. The %Bi-2223 and the %Bi-2212 contained in the x = 0.00 sample were 25.77 % and 74.23 %, respectively. The relatively high value of %Bi-2223 phase might suggest that the Bi-2223 phase was dominant and the sample preparation condition was nearly optimum. As increasing the Na concentration to x = 0.05, the % Bi-2223 was increased to 82.72 % and % Bi-2212 was decreased to 17.28 %. The over-substituted effect was then observed as further increasing x to 0.06 in which the % Bi-2223 was decreased to 81.18 %. The results might reveal that the optimally substituted value of x was about x = 0.05.

In order to analyze more information about changes in the grain sizes, the Debye Scherrer equation was applied [9]: $d = 0.9\lambda/(\Delta\theta\cos\theta_B)$, where d was the size needed to be calculated, λ was the wavelength of the X-ray CuKα radiation, and $\Delta\theta$ was the full width at half maximum of the Bi-2223 peak at the angle θ_B (half of the 2θ value shown in Figure. 1). The calculated results were also given in Table. 1. The increases in the crystal size might evidence that the Na substitutions positively affected the formation of the Bi-2223 crystal. The possible reason for that was attributed to the fact that the Na-substitution reduced the melting point of the BSCCO sample, which led to the increased crystal growth speed basing on the development of liquid phase with a small amount.

Surface morphologies of the fabricated samples were investigated by using the scanning electron microscopy (SEM) as provided in Figure 2. Typical SEM micrographs showed that all samples contained two type of grains: plate-like and needle-like those belonged to the Bi-2223 and Bi-2212 superconducting phases, respectively [2,4]. The Bi-2223 crystals were found to be parallel to the ab plane while the Bi-2212 ones were extended along the c-axis. All samples also exhibited the presence of Ca_2PbO_4 impurity phase, which was detected in form of sphere-like grains randomly distributed over the plates.

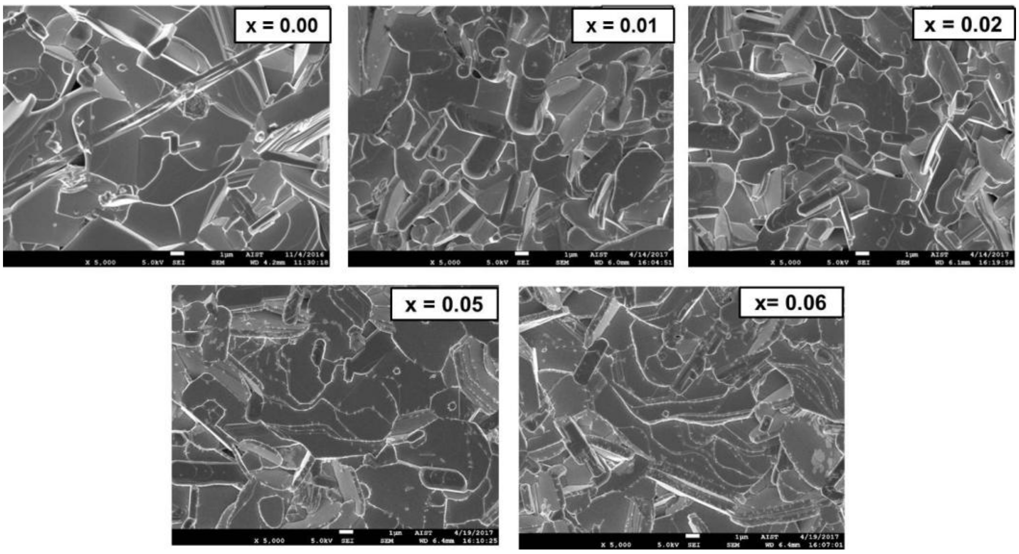

Figure 2. Surface SEM images of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples.

Among the two phases, the Bi-2223 has been proved to act as the dominant in determining superconducting properties of the BSCCO system. The average size of the Bi-2223 grains was estimated to vary as increasing Na concentration as revealed in Figure 3. The variation was compared to be similar to that of %Bi-2223 obtained from XRD results. In addition, the Na-substituted samples exhibit the less porosity, which might indicate the improvement of inter-connectivity between grains.

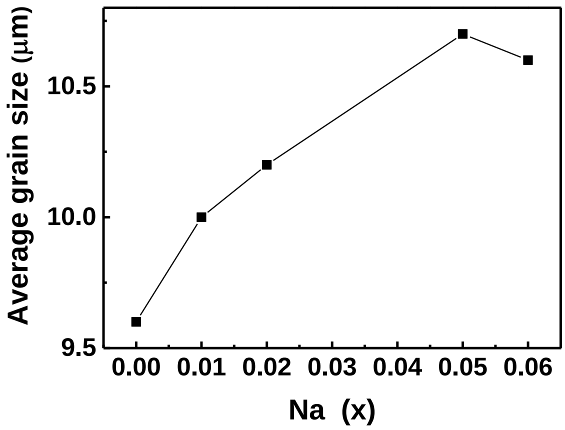

Figure 3. Variation of the average grain size with Na content

The temperature dependence of the resistance of the polycrystalline $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples is graphically provided in Figure 4.

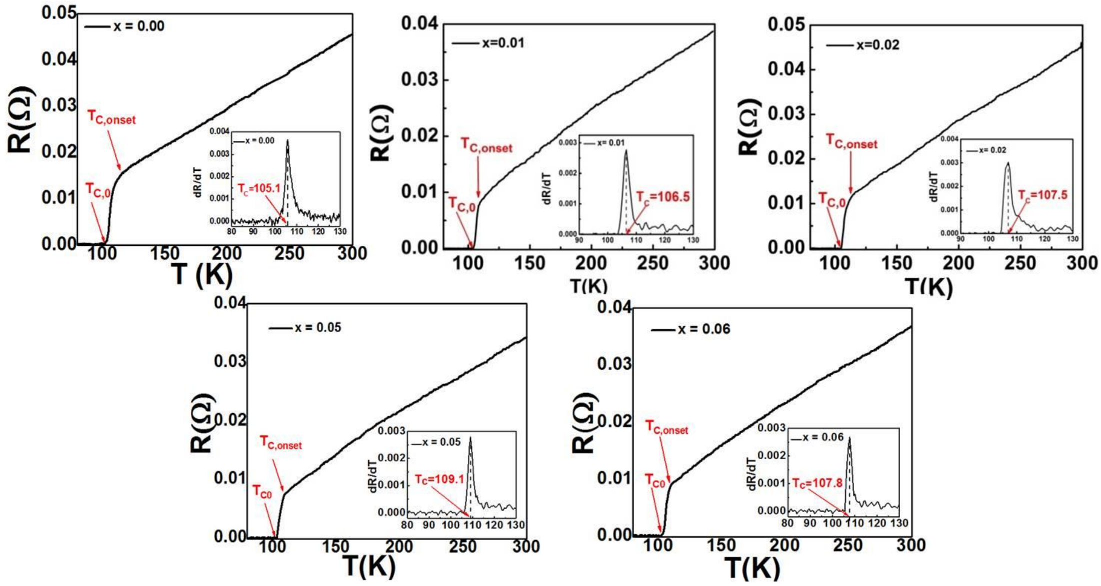

Figure 4. Temperature dependence of resistance of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples. The corresponding derivatives of resistance dR/dT against temperature are given in the inset.

All experimental data show the metallic behavior of the resistance at high temperature region. As decreasing temperature, a transition to the superconducting state occurred. Two transition temperatures consisting of onset critical transition ($T_{c,onset}$) and zero critical transition ($T_{c,0}$) were applied to determine the superconducting transition region. The physical meaning of the two transition temperatures was summarized as the followings: ($T_{c,onset}$) was attributed to the intra-granular transition while ($T_{c,0}$) was corresponded to the inter-granular transition. The transition width (ΔT_c) implying the weak links at grain boundaries was also estimated as $\Delta T_c = T_{c,onset} - T_{c,0}$. Variations of the parameters as a function of the Na content are listed in Table. 2.

Table 2. Variations of the onset critical temperature ($T_{c,onset}$), zero critical temperature ($T_{c,0}$) and transition width (ΔT_c) in the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples

Na (x)	$T_{c,onset}$ (K)	$T_{c,0}$ (K)	ΔT_c (K)	Hole concentration (p)
0.00	112.4	101.6	10.8	0.12589
0.01	112.0	103.5	6.8	0.13325
0.02	112.0	106.0	6.0	0.13453
0.05	112.7	107.5	5.6	0.1354
0.06	112.2	104.0	7.2	0.1343

As revealed in the Table 2, for the x = 0.00 sample, the values of $T_{c,onset}$ and $T_{c,0}$ were observed to be 112.4 K and 101.6 K, respectively. As increasing the Na content up to the level of x = 0.05, the value of $T_{c,0}$ was monotonically increased to 107.5 K, while the value of $T_{c,onset}$ was almost unchanged. The corresponding reduction in the value of ΔT_c indicated that the weak link between the Bi-2223 grains was obviously decreased due to the development of the Bi-2223 grains themselves. Beyond x = 0.05, the slight degradation of the superconducting property was found. The $T_{c,0}$ was decreased to 104.0 K and ΔT_c was increased to7.2 K. All in all, it is worth to say that the substitution of Na into Ca site was favorable for the velocity of the Bi-2223 phase.

The behaviors of the superconducting property of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples were likely to be related to the change in the volume fraction of the Bi-2223. The comparison results were exhibited in Figure 5.

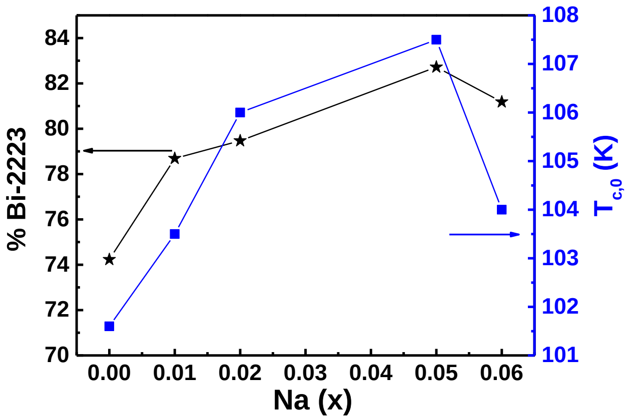

Figure 5. A closely correlation of changes in the zero critical temperature and volume fraction of Bi-2223 of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples

Theoretically, the variation of the value of $T_{c,0}$ was strongly correlated to the hole carrier concentration (p) in the Cu-O_2 plane. The theoretical calculation of p was done by the following equation [5]:

$$p = 0,16 - \left[\left(1 - \frac{T_{C0}}{T_{C,onset}}\right) / 82,6\right]^{1/2} \qquad (3)$$

The calculated results were clearly gathered in Table 2 and plotted in Figure 6. It would be said that $T_{c,0}$ was parabolically dependent on the hole concentration, which was compared to be in agreement with other reports [5,7].

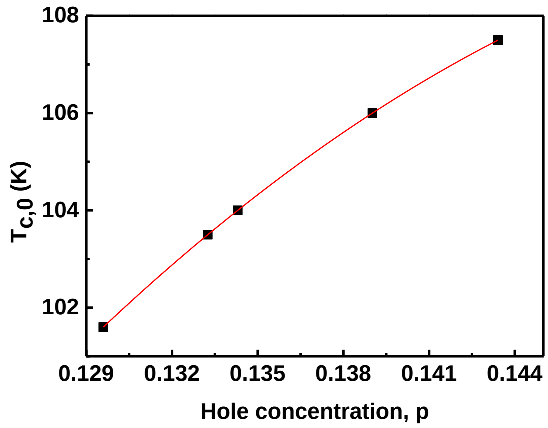

Figure 6. The zero critical temperature versus hole concentration of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples

A sensitive methodology to analyze the relation between the transition temperatures and the structural disorders was examining the variation of $T_{c,0}$ as a function of the residual resistance ratio (RRR) parameter. The RRR defined by R(300K)/R(120 K) has been applied as a measure of sample quality [10]. The results are presented in Figure 7.

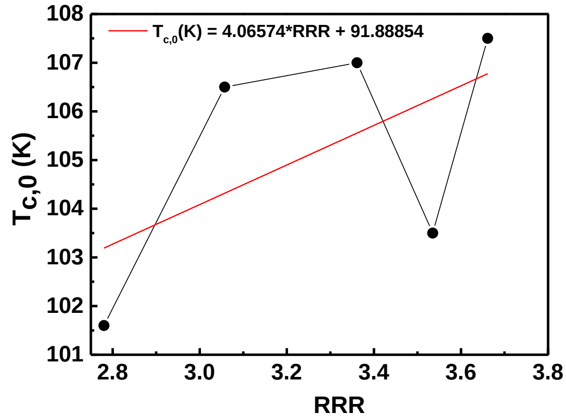

Figure 7. The relation between the zero critical temperature and the RRR of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples

It would be seen that $T_{c,0}$ was somehow proportional to the RRR, except for the x = 0.01 sample. Particularly, an increase in the value of R(120 K) was possibly induced by the increase in impurity scattering in the BPSCCO lattice/ or increase in the lattice strain. Hence, the degradation of the zero critical temperature was obtained. According to Testardi's report, the empirical relation between $T_{c,0}$ and RRR was discussed in details [11]. In our samples, the dependence of $T_{c,0}$ on the RRR was observed, which could be fitted approximately by using a linear function.

3. CONCLUSIONS

In the present work, the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ samples (with x was ranged from 0.00 to 0.06) were fabricated by using the conventional solid state reaction technique. The structural properties of the samples examined by using XRD and SEM measurements showed that Na-substitution enhanced formations of the Bi-2223 phase. The highest volume fraction (%Bi-2223) of 82.72, largest grain size of ~ 10.7 μm and a remarkable reduction of porosity were obtained in the x = 0.05 sample. The temperature dependence of resistance of the samples were measured by using the standard four probe measurements. Variations of $T_{c,0}$ on the Na content were found, which was similar to those of %Bi-2223. As a result, improvements of $T_{c,0}$ in the samples were attributed to the enhanced formation of the Bi-2223 phase. Morveover, the parabolic dependences of $T_{c,0}$ on the hole carrier concentration in CuO_2 plane, and on the RRR were quantitatively analyzed. The samples having higher hole concentration and higher RRR show higher $T_{c,0}$.

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