Modification of the sperconducting parameters of Bi-Sr-Ca-Cu-O by iodine intercalation

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We investigated the superconducting parameters of iodine-intercalated BiSrCaCuO high-temperature superconducting materials. While for samples containing a significant amount of $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) iodine intercalation results in the dramatic decrease of the superconducting parameters, it was found that for samples with a nearly single $Bi_2Sr_2Ca_2Cu_3O_{10-y}$ (Bi-2223) phase these parameters can increase. We argue that this different behavior of the superconducting parameters is the result of a different doping regime, and can be explained based on the parabolic dependence between T_c and the number of holes per CuO_2 layer. Iodine intercalation appears to be an efficient way to bring the usually under-doped superconductor to its optimal T_c and flux pinning properties.

1. Introduction

Bi-based high-temperature superconducting cuprates of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (n=1(Bi-2201), 2(Bi-2212), 3(Bi-2223)) are known to form intercalation compounds by accepting halogen (I_2, Br_2, IBr) between the weakly coupled double BiO layers [1-4]. It was found that iodine intercalation leads to the increase of the distance between the layers by 3.6 Å for each Bi-O bi-layer and, for $n = 1$ and $n = 2$, this decreases the transition temperature T_c. It is supposed that for n = 3 the change in T_c depends considerably on the preparation conditions [5]. The proposed semi-empirical interpretations of the experimental results are based on the increase of the c-axis length, which results in the weakening of the coupling between the superconducting CuO_2 layers in adjacent unit cells [2,6], and on the transport of holes from the intercalated iodine to the CuO_2 layers [5,6]. The effect of iodine intercalation has been most intensively studied in the case of Bi-2212 (see ref. [6,7]). The investigation of the iodine intercalated Bi-2223 phase was limited to structural studies and some resistive and diamagnetic transition measurements on bulk samples [3,5,8]. In this work we analyze the influence of iodine intercalation on the superconducting properties of the samples with different amount of Bi-2223 and Bi-2212.

2. Experimental

The samples were prepared by using a standard solid-state reaction method. Bi_2O_3, PbO, $CaCO_3$ and CuO powders were mixed in the ratio Bi:Pb:Sr:Ca:Cu = 1.7:0.4:1.5:2.5:3.6 for sample 1 and in the ratio Bi:Pb:Sr:Ca:Cu = 1.8:0.4:2:2:3 for samples 2. The precursor powders for samples 3 and 4 were obtained from $SrCO_3$, $CaCO_3$ and CuO powders mixed in the ratio Sr:Ca:Cu = 2:2:3. The obtained powders were pressed into $9 \times 9 \times 3$ mm^3 pellets at 0.75 GPa and calcined with some intermediate grindings at temperatures between 924-950 ^{o}C for 85 h; Bi_2O_3 and PbO powders were added in the obtained precursor to obtain the ratio between components Bi:Pb:Sr:Ca:Cu = 1.8:0.4:2:2:3

All the presintered powders were pressed into $3 \times 3 \times 10$ mm^3 pellets at 0.75 GPa and calcined at 815 ^{o}C for 20 h in air, reground and pressed again into $3 \times 3 \times 10$ mm^3 pellets at 0.75 GPa. Finally, the sintering thermal treatment was performed in air at 848 ^{o}C for 300 h for sample 1, 240 hours for samples 2, and for 330 h for samples 3 and 4.

For the intercalation process the sintered pellets were cut into two pieces: 1V and 1I, 2V and 2I, 3V and 3I, and 4V and 4I. Each piece was encapsulated in a quartz tube in a vacuum of 10 Pa, the tubes with samples 1I-5I containing some amount of iodine. The thermal treatment was carried out at 170-180 °C for 48 h. From our estimations, the partial pressure of iodine in capsules was 0.1-$0.45 \cdot 10^5$ Pa, depending on the amount of iodine.

X-ray diffraction (XRD) measurements were performed using the CuK_α radiation. The sample morphology was studied by scanning electronic microscopy (SEM). The electrical resistivity was measured by the standard four-probe method, with a transport current of 1.5 mA, using silver paint for electrical contacts. The Seebeck coefficient was measured at room temperature, using the warm point method and a platinum reference. The *ac* susceptibility measurements were performed using the lock-in amplification technique, at a fixed frequency of 5.5 kHz and temperatures T down to 77.3 K. The transport critical-current density J_{ct} was determined at $T = 77.3$ K in zero applied magnetic field, with the voltage criterion of 1 μV/cm.

3. Results and discussion

3.1 XRD and SEM analyses

The XRD patterns for samples 1 and 2 are shown in Fig. 1. It is obvious that the structure of the intercalated Bi-2223 and Bi-2212 phases is expanded along the *c*-axis.

In order to calculate the expansion of the *c*-axis in our intercalated samples, the Miller indices were assigned for the non-intercalated compound, as well as for the intercalated compound. We found the extension of each BiO layer by about 3.4 Å for the both Bi-2212 and Bi-2223 intercalated phases (see Table 1). These values are in good agreement with those given in literature.

Fig. 1. XRD patterns for samples 1, 2 and standard-single Bi-2223 phase sample. (Phase notation: 1- Bi 2223, 1'-intercalated Bi-2223, 2-Bi-2212, 2'-intercalated Bi-2212, 3-Ca$_2$PbO$_4$, 4-CuO, 5-Ca$_2$CuO$_3$, 6-(Sr,Ca)$_{14}$Cu$_{24}$O$_x$, 7-Bi-2201.

The total (*f*), non-intercalated (f_{ni}), and intercalated volume fraction (f_i) of the high-temperature superconducting Bi-2223 phase were estimated using the equations

$$f_{ni} = \frac{A(0010)_{2223}}{A(0010)_{2223} + A(006)_{2223} + A(008)_{2212} + A(005)_{2212}}, \quad (1)$$

$$f_i = \frac{A(006)_{2223}}{A(0010)_{2223} + A(006)_{2223} + A(008)_{2212} + A(005)_{2212}}, \quad (2)$$

$$f = f_{ni} + f_i, \quad (3)$$

where $A(0010)_{2223}$ and $A(008)_{2212}$ represent the peak area for the reflections of non-intercalated phases $(0010)_{2223}$ and $(008)_{2212}$, and $A(006)_{2223}$ and $A(005)_{2212}$ represent the peak area for the reflections of intercalated phases $(006)_{2223}$ and $(005)_{2212}$. The *f* values of the investigated samples are 95 %, 45 %, 78 %, 30 %, 80 %, 91 % and 93 % for samples 1I, 2I, 4I, 2 as-grown, 3V, 3 as-grown and 4 as-grown, respectively.

The Bi-2212 and Bi-2223 phases in samples 2 are stage-I (100 %) intercalated, the Bi-2223 phase in sample 1 is nearly stage-I (100 %) intercalated, while Bi-2223 in samples 3 and 4 are partially intercalated. By comparing the *f* values for samples 2-as-grown and 2I, we notice a large difference, namely before intercalation *f* = 30 %, whereas after intercalation *f* = 45 %. This indicates the destruction of the superconducting phases in the intercalated samples (from the point of view of crystallography), and the Bi-2212 phase was more

affected. In the case of the nearly single Bi-2223 phase sample 4 *f* decreases after intercalation, suggesting the decrease of the amount of Bi-2223, as well.

SEM observations and electron diffraction spectroscopy (EDS) measurements confirmed the existence of iodine inside our samples: more for sample 2, for example (stage-I iodine intercalation), and less for sample 4 (incomplete intercalation). SEM revealed no morphological modifications in the intercalated samples.

Table 1. Structural data of iodine processed samples.

Sample	Remarks
1I	f_i^{2223} = 85 %, c_i (Å) = 22 ± 0.02; f_{ni}^{2223} = 10 %, c_{ni} (Å) = = 18.6 ± 0.05 $f_i^{2212} + f_{ni}^{2212}$ = 5 %
2I	f_i^{2223} = 45 %, c_i (Å) = 21.98 ± 0.01; f_i^{2212} = 55 %, c_i (Å) = = 18.85 ± 0.1
4I	f_i^{2223} = 18 %, c_i (Å) = 22 ± 0.11; f_i^{2212} = 22 %, c_i (Å) = = 18.80 ± 0.1 f_{ni}^{2223} = 60 %, c_{ni} (Å) = 18.58 ± 0.05

3.2 Transport measurements

R(T) measurements

Figs. 2a and 2b illustrate the *T* dependence of the resistance $R(T)$ normalized to $R^{300\ K}$ for samples 2 and 3, respectively. The superconducting parameters determined from the $R(T)$ variation are given in Table 2. After iodine intercalation, $T_c^{\rho=0}$ decreases for samples 2 and 3, slightly decreases for sample 1, and increases for sample 4. T_c decreases for samples 2 and 3, practically does not change for sample 1, whereas for sample 4 it increases after intercalation.

Fig. 2. Temperature dependence of the ratio R(T)/R$^{300\ K}$ for as-grown, vacuum annealed and iodine intercalated samples 2 (a) and 3 (b).

For all samples J_{ct} decreases, but it is more affected for samples containing a large amount of Bi-2212. It is worthy to mention that T_c (determined at the midpoint of the resistive transition) characterizes the grains, as well, whereas $T_c^{R=0}$ and J_{ct} are highly influenced by the strength of the weak links between the grains. Intercalation strongly affects J_{ct}, due to the high vulnerability of the grain edges, which is confirmed by Seebeck coefficient measurements.

The large number of specimens investigated in this work allowed as concluding that for samples containing a large amount of Bi-2212 phase the supercurrent transport parameters are strongly affected by iodine intercalation (representative sample 2). For the nearly single Bi-2223 phase specimens, one can distinguish three situations, in which the transport parameters slightly decrease (representative sample 3), practically do not change (representative sample 1), or increase (characteristic sample 4).

As can see in Table 2, for samples containing a large amount of Bi-2212 the superconducting parameters are more strongly affected by iodine intercalation than by vacuum annealing. In the case of nearly single Bi-2223 phase specimens, the difference between the effect of iodine intercalation and vacuum annealing depends on the above mentioned three situations.

Table 2. Transport and thermoelectric parameters.

Sample no.	T_c (or T_c^{2223}) (K)	$T_c^{\rho=0}$ (K)	Seebeck coefficient (μV/K)	J_{ct} (A/cm^2)
1I	110.3	87	3.07	0.36
2I	109	91.8	8.11	0.22
3I	107.3	94.7	7.87	1.55
4I	110.9	107.6	4.56	20.00
2V	113.5	109.8	5.58	18.80
3V	108.4	96.0	8.38	0.15
1 as-grown	110.6	100.1	2.70	0.50
2 as-grown	116.4	113.4	1.20	33.10
3 as-grown	110.1	100.2	3.31	17.30
4 as-grown	109.7	105.5	3.37	27.60

Seebeck coefficient measurements

It is known that the thermopower of under-doped Bi-based superconductors in the normal state is usually positive, and its value decreases by increasing the number of holes. The values of the Seebeck coefficient α are given in Table 2. It can be seen that the as-grown pellet 2 has the smallest α value, which indicates a higher carrier concentration and higher oxidation states of the superconducting CuO$_2$ layers. Indeed, this is in agreement with the high supercurrent transport parameter values of the as-grown samples 2 obtained from the $R(T)$ curves. As would be expected, vacuum annealing leads to the increase of the coefficient α for all samples, since after vacuum annealing the specimens are more under-doped.

If we compare the coefficients α of intercalated and vacuum-annealed samples (Table 2), an apparent contradiction arises. Namely, α for the intercalated samples is quite high. In some cases, after intercalation α becomes even higher than the value measured for the corresponding vacuum annealed specimen. However, this contradiction can be solved by considering that the high α for the intercalated samples is a result of a high intercalation level at the grain edges. This is supported by the behavior of sample 1, for which T_c changes

insignificantly after intercalation, whereas $T_c^{\rho=0}$ decreases by ~13 K.

As a rule, α tends to be smaller, even negative, for as-grown samples with a large amount of Bi-2212, whereas for the as-grown nearly single Bi-2223 phase specimens α always have higher, positive value. Indeed, it is well known that for similar treatment conditions the Bi-2212 phase tends to be more (over-) doped than the Bi-2223 phase. It is still unclear if the low α values of our multiphase samples are caused by Bi-2212 itself, or are due to the Bi-2223 phase, with a doping level influenced by the surroundings rich in Bi-2212 during the thermal treatment.

Therefore, our samples with a large amount of Bi-2212 are optimally doped or slightly over-doped, whereas the nearly single Bi-2223 phase specimens are slightly under-doped.

3.3 ac susceptibility measurements on ground samples

As shown above, $T_c^{\rho=0}$ and J_{ct} decrease for all samples after iodine intercalation, since the grain edges are strongly affected. The influence of iodine intercalation on the grains can be detected using *ac* susceptibility measurements. It is better to perform such measurements on ground samples, for which the inter-granular signal is highly diminished.
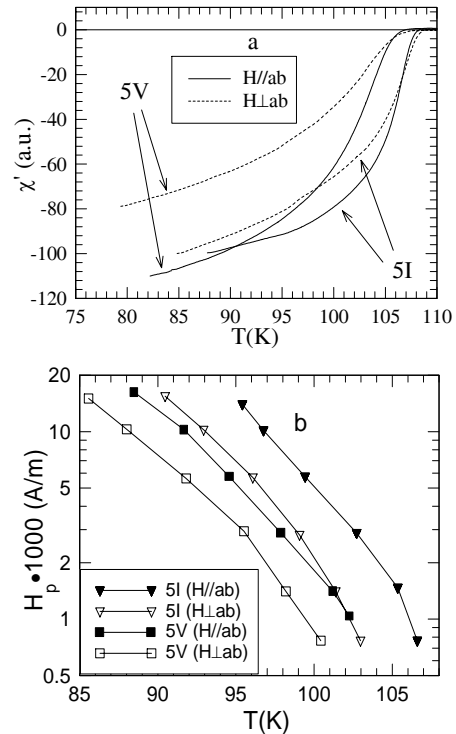

Fig. 3. The in-phase ac susceptibility measurements performed on samples 5V and 5I in ac field of H_{ac}=3.2 A/m (zero static field) for both H//ab and the H⊥ab directions (a). The temperature dependence of H_p determined from the peak position of out-of-phase measurements in ac magnetic field with the amplitude H_{ac} = 100A/m at different values of the superimposed static field (b).

We chose an as-grown sample 5, which was very similar to as-grown samples 1, 3 and 4, with the nearly single Bi-2223 phase in the slightly under-doped regime and with $T_c \approx 109$ K. The sample 5 was cut into two pieces, which were ground and pressed to obtain a certain degree of preferential grain orientation. One of the pellets (5V) was vacuum annealed and another (5I) was intercalated.

Fig. 4a shows the in-phase ac susceptibility measurement results obtained for these two samples in an *ac* field $H_{ac} = 3.2$ A/m oriented parallel to the pellet surface ($H//$ab) and perpendicular to it ($H\perp$ab). We determined T_c from the onset of the diamagnetic signal, which leads to $T_c = 107.5$ K ($H//$ab) and $T_c = 106.9$ K ($H\perp$ab) for sample 5V, and $T_c = 109.2$ K ($H//$ab) and $T_c = 108.8$ K ($H\perp$ab) for sample 5I. T_c of slightly under-doped BiSrCaCuO sample (Bi-2223 phase) has higher values after iodine intercalation than after vacuum annealing.

Fig. 4b illustrates the T variation of the field of full penetration H_p, determined from the peak position of out-of phase signal, for the same 5V and 5I samples. The $H_p(T)$ curves for the intercalated sample are shifted towards higher fields comparative to its non-intercalated (vacuum annealing) pair, which suggests a stronger flux pinning (intragranular critical current density, J_{cg}). The position of the $H_p(T)$ curves for the sample 5I are close to the position of the best curve obtained by us among the similar as-grown bulk samples, suggesting the tendency of this parameter to reach its optimal value after intercalation for under-doped nearly single Bi-2223 phase samples.

In the following we summarize all the results obtained from transport and ac susceptibility measurements.

a) *Samples with a large amount of Bi-2212 phase.* T_c, J_{cg} and the transport parameters which characterize the weak links clearly decrease in the iodine intercalated samples, and the superconducting parameters of the as-grown samples are more strongly affected by iodine intercalation than by vacuum annealing. The as-grown samples were in the optimal doping or slightly over-doping regime.

b) *Samples with the nearly single Bi-2223 phase.* T_c and J_{cg} tend to increase after iodine intercalation, and the transport parameters which characterize the weak links appear to be more strongly affected by vacuum annealing than by iodine intercalation. It is important to remind that the as-grown samples are in the slightly under-doped regime.

Therefore, the difference between the obtained results on samples (a) and (b) after intercalation and vacuum-annealing would rise from the *different doping level of as-grown samples.*

It was shown that charge transfer is an important aspect of intercalation in the high-temperature superconductors, consistent with the XPS data [5], which showed an ionic character for the intercalated iodine. Therefore, we can explain the effect of iodine intercalation on our samples with different oxygen content based on the parabolic dependence between T_c and the number of holes per CuO$_2$ layer. According to Pooke *et al*. [5], qualitatively, for materials lying close to, or to the right of the peak in T_c (over-doped region), significant hole doping will lead to a T_c decrease. The results for sample 2 (with large a amount of Bi-2212 phase) are consistent with this supposition since the charge transfer from the intercalated iodine to the CuO$_2$ layer takes place. For materials starting

in the under-doped side, the same intercalation process increases T_c, the tendency observed for sample 4 (with nearly single Bi-2223 phase). Therefore, since the samples with a large amount of Bi-2212 phase are optimally doped (or slightly over-doped), their superconducting parameters are suppressed by iodine intercalation. On the other hand, as the samples with the nearly single Bi-2223 phase are under-doped, their superconducting parameters tend to the optimal values after iodine intercalation. This suggestion is confirmed by the behavior of these two groups of samples after vacuum annealing.

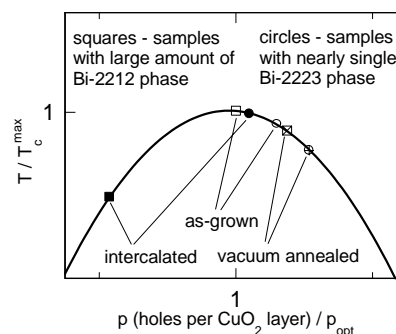The described situation becomes clearer from its schematic illustration in Fig. 4.

Fig. 4. Schematic illustration of the general trend of T_c of as-grown BiSrCaCuO samples after intercalation and vacuum annealing.

Based on Fig. 4 and on the measured superconducting parameters, the expected effect of iodine intercalation and vacuum-annealing is given in Table 3.

Table 3. The suggestion of the comportment of all investigated samples after intercalation and vacuum annealing.

Sample	Doping regime			
	As grown	After intercalation	After vacuum-annealing	Remark
1	slightly under-doped	higher doping level but still under-doped		
2	optimal doped	over-doped	under-doped	
3	slightly under-doped	slightly over-doped	more under-doped	The decrease of T_c for sample 3I seems to be due to the shift of this sample towards the over-doped region
4	slightly under-doped	optimal doped		Besides the T_c increase, the important confirmation of the fact that the sample 4I is in optimal doping regime is the increase of $T_c^{\rho=0}$ after intercalation
5	slightly under-doped	close to optimal doping	more under-doped	

Thus, in our opinion, the superconducting parameters of the samples with a majority of Bi-2212 phase are strongly affected by iodine intercalation because these samples were in the optimal or over-doped state prior intercalation. On the other hand, since the as-grown samples with the majority of Bi-2223 are in the under-doped state, their superconducting parameters tend to optimal values after iodine intercalation.

4. Conclusions

In summary, we have investigated the superconducting properties of the iodine-intercalated BiSrCaCuO high-temperature superconducting system. From transport measurements, it was found that the effect of iodine intercalation on the superconducting parameters is larger for samples containing the Bi-2212 phase (which are optimally doped or slightly over-doped before intercalation) than for samples with the majority Bi-2223 phase (which are in a slightly under-doped state before intercalation). We have qualitatively explained the effect of iodine intercalation on the samples with different oxygen content using the parabolic dependence between T_c and the number of holes per CuO_2 layer. An important conclusion for practical applications is that the iodine intercalation is an easy way to bring the superconductor to its optimal T_c and flux pinning properties, if this superconductor is in an under-doped region before intercalation.

Acknowledgments

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