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LETTER TO THE EDITOR

Iodine Intercalation in $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$: Evidence of Hole Transfer from Iodine to Copper–Oxygen Sheets

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We have successfully intercalated iodine between the Bi–O layers of the semiconducting $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$. X-ray diffraction and thermogravimetric analysis confirmed the formation of a stage-1 intercalated compound, $IBi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$. Upon intercalation, the compound became superconducting, indicating that there is a modest transfer of holes from iodine located in Bi–O layers to Cu–O sheets. © 1994 Academic Press, Inc.

Recently, it has been demonstrated that iodine can be intercalated into $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ superconductors (1–3). The iodine was intercalated in between the Bi–O layers and caused a corresponding expansion along the *c*-axis of 3.6 Å for each Bi–O double layer (4). The intercalated iodine atoms occupied specific sites between Bi–O layers and altered the atomic stacking across the Bi–O layers from the staggered configuration to the vertically aligned one. In general, the iodine-intercalated compounds exhibited lower superconducting transition temperatures than the host materials from which they were fabricated. Faulques and Russo (5) and Trodahl *et al.* (6) investigated iodine-intercalated $Bi_2Sr_2Ca_{n-1}Cu_nCu_2O_x$ ($n = 1, 2$) by Raman spectroscopy and concluded that the iodine in the lattice exists in the form of triiodide ions (I_3^-). Xiang *et al.* (1–3) speculated that the lowering of the T_c is not due to the charge transfer from iodine to the CuO_2 planes but due to the large separation of the superconducting $(CuO_2)_n$ clusters (hence dynamic coupling between them) caused by the lattice expansion for the iodine intercalated material. In contrast to the above explanation, Pooke *et al.* (7) reported that the lowering of T_c is due to the over-doping of holes in the CuO_2 sheets resulting from the transfer of charge from iodine to copper–oxygen sheets.

In order to understand better the effect of iodine intercalation on the superconducting properties of Bi-based superconductors, we decided to investigate the intercalation of iodine in the semiconducting $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$. This phase lies on the semiconductor–superconductor boundary in the system $Bi_2Sr_2Y_{1-x}Ca_xCu_2O_{8+\delta}$. Superconductivity was observed for $Bi_2Sr_2Y_{1-x}Ca_xCu_2O_{8+\delta}$ phases with $x \geq 0.6$, where substitution of M^{2+} for Y^{3+} raised the formal oxidation state of copper above $+2.1$ (8, 9). If one assumes that there exists significant hole donation to the copper–oxygen sheets when iodine is intercalated between Bi–O layers, iodine intercalation in $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$ should render this phase superconducting.

The pristine $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$ samples were prepared by a solid-state reaction of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO at 875°C for 24 hr. The powder was reground and heated again as pellets at 900°C for 12 hr. The X-ray diffraction pattern indicated formation of a single-phase product with 2212-type structure. The iodine intercalation was performed through a direct gas phase reaction of elemental iodine with $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$ at 175°C for 72 hr in a vacuum-sealed Pyrex tube. The test for superconductivity was made by the AC mutual inductance technique. Electrical resistivity measurements were executed by the standard four-probe technique.

Figures 1a and 1b show the X-ray diffraction patterns for pristine and iodine-intercalated $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$, respectively; the lattice constants are listed in Table 1. The *c*-lattice dimension for the pristine phase is ~30.3 Å, whereas that for the iodine-intercalated compound is ~37.5 Å, showing a lattice expansion corresponding to ~3.6 Å for each Bi–O layer. This is consistent with previous reports on iodine intercalation of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (2–4). Iodine intercalation changes the stacking of the basic building blocks in the unit cell of the pristine host materials from a staggered sequence (two identical basic building blocks shifted by $\frac{1}{2}$ *a* with respect to each other) to an aligned one; the new unit cell is primitive (space group *Pma2*, with a single basic block per unit cell) (4).

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FIG. 1. X-ray diffraction patterns for (a) pristine and (b) iodine-intercalated $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$.

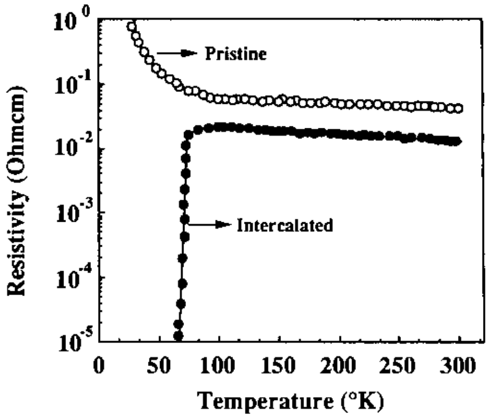

FIG. 2. Electrical resistivity data for pristine and iodine-intercalated $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$.

Prior to intercalation, the oxygen content in the pristine sample was determined by iodometric titration. The formal valence of copper derived from the oxygen content, assuming all the Bi ions to be in trivalent state, is +2.08 (±0.03). The weight loss observed from the thermogravimetric analysis for the intercalated compound, after applying a correction for the weight loss due to the pristine sample, indicated that the ratio of iodine to $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$ is close to 1 : 1. This again confirms the formation of a stage-1 intercalate. Figure 2 shows the electrical resistivity data for the pristine and stage-1 intercalated $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$. The pristine compound showed semiconducting behavior in good agreement with the literature data (8, 9). Upon intercalation, the compound clearly became superconducting with a T_c onset close to 76 K. The intercalation experiment was repeated three times using three different batches of $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$ to ensure reproducibility. In all cases the intercalated phases exhibited superconducting behavior with transition temperatures varying within 5°C. The iodine intercalation was also performed with samples in the semiconducting region of $Bi_2Sr_2Y_{1-x}Ca_xCu_2O_{8+\delta}$, where $x = 0$ and 0.4. The formal valence of copper derived from analytical data for the $x = 0$ phase is +1.85 (±0.03), whereas that for the $x = 0.4$ phase is +2.02 (±0.03). In both cases, the compounds remained semiconducting after iodine intercalation.

TABLE 1
X-Ray Data for Pristine and Iodine-Intercalated $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{8+\delta}$

Compound	Space group	Lattice parameters		
		a(Å)	b(Å)	c(Å)
Pristine	*Amaa*[a]	5.412(2)	5.419(2)	30.35(1)
Iodine-intercalated	*Pma*2	5.409(3)	5.415(3)	18.78(1)[b]

[a] Subcell lattice parameters. Superstructure ignored.
[b] 2 × c for A-centered cell.

Raman spectra (6) for iodine-intercalated $Bi_2Sr_2CaCu_2O_{8+\delta}$ showed that iodine exists as $(I_3)^-$; this corresponds to 0.33 holes/iodine (or 0.16 holes for each copper–oxygen sheet), if one assumes complete charge transfer from iodine to copper. The fact that the $x = 0$ and 0.4 phases remained semiconducting upon iodine intercalation indicates that only a modest transfer of charge from iodine to Cu–O sheets occurs; it is likely that the rest of the charge is donated to Bi–O layers, where the Bi^{3+} can be oxidized to Bi^{4+}. A detailed investigation on the intercalation of iodine in the entire range of $Bi_2Sr_2Y_{1-x}Ca_xCu_2O_{8+\delta}$ solid-solution systems is being completed and will be reported elsewhere.

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Note added in proof. Raman spectra of iodine-intercalated $Bi_2Sr_2Y_{0.5}Ca_{0.5}Cu_2O_8$ showed a strong bond at 110 cm^{-1} indicating the presence of iodine as I_3^- ions.

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