Iodine intercalation of a high-temperature superconducting oxide

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INTERCALATION compounds are formed by inserting guest atomic or molecular species between weakly bound (usually by van der Waals forces) slabs of host materials without changing the inner crystal structure of the individual slabs. The best-known examples of host materials are graphite and the transition metal dichalcogenides[1]. These compounds can be made with different stage index n, where n denotes the number of slabs between adjacent intercalated layers. Intercalation provides a unique, well controlled approach to changing the physical and electronic properties of host materials over a wide range[1]. If intercalation can be adopted in the layered high-transition-temperature (high-T_c) superconductors, it could lead to the ability to engineer their properties, with a view to investigating the mechanism responsible for high-T_c superconductivity, improving the superconducting properties of the pristine materials, and developing new high-T_c superconductors and superconducting devices. We report here the successful synthesis and preliminary physical characterization of a stage-1 iodine-intercalated high-T_c superconductor, $IBi_2Sr_2CaCu_2O_y$.

Intercalation is possible only when the binding between the slabs of the host material is very weak. Several of the high-T_c oxide superconductors fall into this class. For example, $Bi_2Sr_2CaCu_2O_8$ crystals have a micaceous structure with anisotropic binding, allowing the crystals to be easily cleaved between the double [Bi–O] layers[2]. The interplane bond length between the double [Bi–O] layers is 3.7 Å, whereas the intraplane Bi—O bond length is 2.3 Å (ref. 3).

We have intercalated iodine between the [Bi–O] planes of $Bi_2Sr_2CaCu_2O_8$, yielding a new stage-1 compound in which the c axis is increased by 23% over the pristine unit-cell dimension. The stoichiometry of the saturated material is $IBi_2Sr_2CaCu_2O_y$; it is a bulk superconductor with transition temperature of 80 K.

To prepare the samples, iodine and high-quality single crystals of $Bi_2Sr_2CaCu_2O_8$ (with transition temperatures ranging from 82 to 90 K) were sealed in pyrex tubes under a vacuum of $<10^{-3}$ torr and placed in uniform-temperature furnaces. For temperatures less than 100 °C and times shorter than six days, the resulting compounds were not single-phase but a mixture of stage-1 and pristine materials. For temperatures over 250 °C, the resulting materials were mixtures of stage-1 and higher-stage phases. Single-phase stage-1 materials were obtained for temperatures in the range 150–200 °C and times of 10–15 days. Unlike most graphite intercalation compounds, the iodine-intercalated oxide superconductor is stable in air, which greatly simplifies characterization of physical properties and may be useful in applications. To determine the amount of iodine introduced into the host material, we studied both the weight change and scanning-electron-microscope X-ray fluorescence of the single-phase stage-1 material. Both methods yielded a 1:1 ratio of I to Ca, that is, the resulting material is $IBi_2Sr_2CaCu_2O_y$.

The X-ray diffraction patterns of highly oriented (along the c axis) crystals of $Bi_2Sr_2CaCu_2O_8$ and $IBi_2Sr_2CaCu_2O_y$ are shown in Fig. 1a and b, respectively. The c-axis unit-cell dimension for the pristine material is 30.82 Å, whereas that for $IBi_2Sr_2CaCu_2O_y$ is 37.78 Å, corresponding to an increase of ~7 Å, or 23%. The $IBi_2Sr_2CaCu_2O_y$ material is stage-1 and single-phase to a resolution better than 1%. Because samples intercalated over a period of 10 days have the same structure
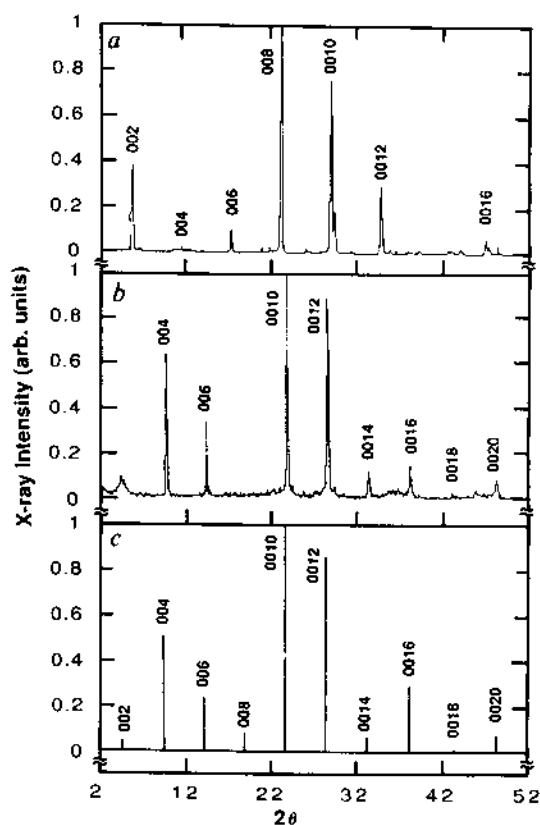

FIG. 1 Highly oriented crystal X-ray diffraction patterns of a, pristine $Bi_2Sr_2CaCu_2O_8$ and b, $IBi_2Sr_2CaCu_2O_y$. c, Predicted diffraction pattern of $IBi_2Sr_2CaCu_2O_y$ assuming that the iodine is intercalated between [Bi-O] bilayers.

as samples intercalated over 15 days, the structures are most likely fully saturated.

For each unit cell of host $Bi_2Sr_2CaCu_2O_8$ there are two intercalated layers of iodine; each iodine layer expands the c axis by ~3.5 Å. To determine whether the intercalated layer lies between the [Bi–O] planes or between the [Cu–O] planes, we calculated the expected relative X-ray scattering intensities for both possibilities. We obtained good agreement between the predicted and experimental intensities by assuming that the iodine layer is between the weakly bound [Bi–O] bilayers. Figure 1c shows the calculated intensity for this configuration; the results should be compared to the experimental data in Fig. 1b. The interlayer [Bi–O]-[Bi–O] spacing is the largest in the $Bi_2Sr_2CaCu_2O_8$ structure (10% larger than the Cu–O interlayer spacing) and is thus the most receptive site for iodine intercalation.

Although iodine intercalation dramatically increases the c-axis unit-cell dimension in $Bi_2Sr_2CaCu_2O_8$, it has little effect on the in-plane a and b dimensions. Figure 2 shows an X-ray powder diffraction pattern for iodine-intercalated polycrystalline $Bi_2Sr_2CaCu_2O_8$. The c-axis unit-cell dimension is 37.8 Å (in agreement with the intercalated single-crystal data), whereas the a and b dimensions are both 5.4 Å, equal to the a and b dimensions of the pristine material[3].

We have characterized the superconducting properties of $IBi_2Sr_2CaCu_2O_y$ by magnetization measurements and, to a lesser extent, by transport measurements. Figure 3 shows the temperature-dependent a.c. magnetic susceptibility $\chi_{a.c.}$ for a single crystal of $IBi_2Sr_2CaCu_2O_y$, obtained at 10 MHz. A sharp superconducting transition is observed at 80 K; this value was consistently obtained for different specimens of $IBi_2Sr_2CaCu_2O_y$, independent of the original T_c of the host material (which ranged from 82 to 90 K). To estimate the superconducting volume fraction in the intercalated material, $\chi_{d.c.}$ was measured using a d.c. SQUID (superconducting quantum interference device). The inset in Fig. 3 shows $\chi_{d.c.}$ data near the superconducting
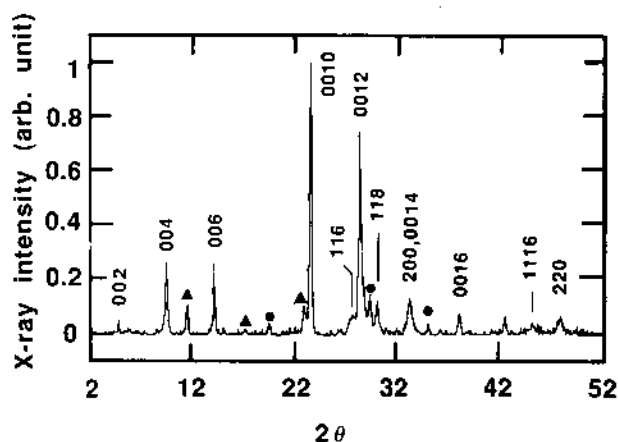
FIG. 2 Powder X-ray diffraction pattern for $IBi_2Sr_2CaCu_2O_y$ indexed to the double-slab unit cell. The triangles and circles identify very small amounts of impurity phase.

FIG. 3 A.c. magnetic susceptibility $\chi_{a.c.}$ of $IBi_2Sr_2CaCu_2O_y$. The transition temperature is 80 K. The inset shows the d.c. magnetic susceptibility $\chi_{d.c.}$ near the transition region; the data indicate bulk superconductivity.

transition. At low temperatures, ~30% of an ideal d.c. Meissner effect is obtained, comparable to that observed for the pristine material. This indicates that $IBi_2Sr_2CaCu_2O_y$ is a bulk superconductor. Preliminary measurements of the electrical resistivity, performed along the ab plane of $IBi_2Sr_2CaCu_2O_y$, showed a nearly linear temperature-dependence in the normal state above T_c (characteristic of the ab-plane behaviour of host compound). The resistivity dropped to zero at T_c.

The band structure[4] of $Bi_2Sr_2CaCu_2O_8$ shows that the density of states at the Fermi energy $N(E_f)$ is dominated by bands derived from the $Cu(3d)$–$O(2p)$ orbitals. Thus, as we expect that the iodine only perturbs the Bi–O bands, there should be a very small effect on $N(E_f)$ and, in turn, on T_c. We would expect a much larger ΔT_c if iodine were intercalated between the [Cu–O] planes. Therefore, band-structure calculations are consistent with our determination of the iodine placement between the [Bi–O] layers.

Based on many studies of the copper oxide superconductors, it has been suggested (see, for example, ref. 5) that only the copper–oxygen planes (square, pyramidal and octahedral) are critical structural components in these high-T_c systems. The secondary structural components are expected to act only as 'charge reservoirs' which control the local charge concentration on the copper–oxygen planes. The superconducting transition temperature is closely related to the effective valence of the Cu atoms in the plane[5].

Assuming that the Bi–O planes do serve as charge reservoirs for the [Cu–O] planes, we would expect iodine intercalation to increase the concentration of holes and therefore increase the carrier concentration and T_c. The observed change in T_c, however, is small and negative, suggesting that the intercalated iodine is not electrically active. It is possible that molecular iodine was intercalated, but further measurements are needed to confirm this.

Knowing the placement of the intercalated iodine layer and the resulting T_c allows us to compare our results with the predictions of theoretical models that focus on interlayer coupling in the high-T_c oxides. The model of Wheatley et al.[6]
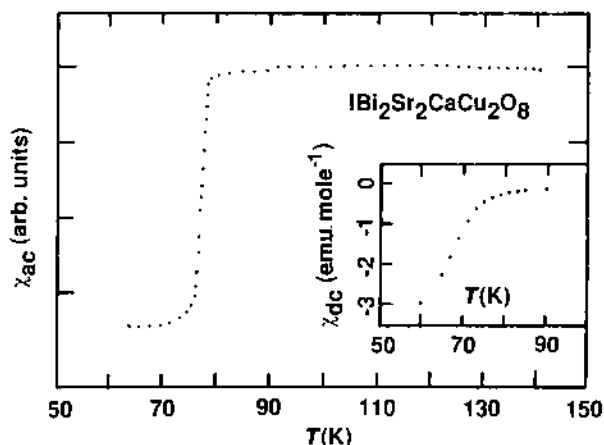
is based on a combination of near-[Cu–O]-plane coupling and next-cell coupling, whereas Ihm and Yu[7] have proposed a model in which only near [Cu–O] planes interact. According to these models, intercalation between the consecutive [Cu–O] layers in $Bi_2Sr_2CaCu_2O_8$ (doubling the spacing there) would reduce T_c drastically, but intercalation between the [Bi–O] layers would change T_c by less than 5 K. Intercalation of the thallium-based oxide superconductors would distinguish between these models, because the model of Ihm and Yu predicts no change in T_c for intercalation between the [Tl–O] layers, whereas the model of Wheatley et al. predicts that T_c would fall sharply.

Another interesting question addressed by intercalation of high-T_c superconductors is whether or not the superconductivity in these materials is two-dimensional, as has been suggested by other experimental studies[8,9]. An excellent example of two-dimensional superconductivity is the TaS_2 intercalation compound with expansion of the c-axis by a few angstroms up to 60 Å (by insertion of organic compounds into host materials)[1]. These compounds still remain superconducting which suggests that the superconductivity is predominantly two-dimensional. In the case of $IBi_2Sr_2CaCu_2O_y$, although there is still insufficient data to draw a firm conclusion, the fact that the insertion of 3.5-Å iodine layer does not drastically affect the T_c of the pristine material implies two-dimensional character of the superconducting processes in this material. □

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