Articles

Metal Iodides: Novel Solution Precursors to Cuprate Superconductors

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$YBa_2Cu_3O_{7-\delta}$ (YBCO) was produced through oxidation of a 1:2:3 mixture of YI_3, $BaI_2 \cdot 2H_2O$, and CuI solids. TGA of the iodides revealed low-temperature oxidation below 600 °C of the iodide precursors to the oxides. Thin oriented films of orthorhombic YBCO were prepared by multiple spin coating, drying, and oxidizing solutions of the same solids mixture in acetonitrile/ethanol on a $SrTiO_3$ single crystal. Confirmation of bulk and film structures were made with the aid of X-ray diffractograms, scanning electron and optical microscopy, and resistivity measurements. Typical "zero resistance" behavior at 90 K was observed for the iodide precursor derived YBCO.

Introduction

Solution or sol/gel processing of oxide ceramics has been the subject of intense research for over 15 years,[1] long before the discovery of the cuprate superconductors.[2] Solution processing of ceramics has many advantages. Among these are (1) the ability to obtain and maintain chemical purity, (2) the ability to produce thin films through centrifugal solution processing, and (3) the propensity to lower processing temperatures.[3] For these reasons, researchers began exploring solution processing of the cuprate superconductors soon after their discovery. In addition to aqueous routes involving nitrate precursors,[4] metalloorganic precursors such as citrates,[5] alkoxides,[6] oxalates,[7] neodecanoates,[8] trifluoroacetates,[9,10] and β-diketonates[6] have been described in the literature.

In the case of cuprate superconductors, metalloorganic precursors can lead to metal carbonates due to the formation of carbon dioxide during oxidation processing of the carbon-containing precursor ligands attached to the metal ions. Usually, the ligand is removed by hydrolysis with excess water followed by precipitation of the resulting metal hydroxide. However, fatty acid esters ligands cannot easily be removed by oxidation and/or hydrolysis. In the case of $YBa_2Cu_3O_{7-\delta}$ superconductors, temperatures in excess of 900 °C are often used to decompose intermediate barium carbonate which can interfere kinetically with the formation of pure YBCO. For these reasons, non-carbon-containing organic-solvent-soluble precursors which would convert to oxides at low temperatures were sought. Earlier developments suggest that iodide salts meet these requirements.[11]

Iodide salts have been used as CVD precursors to oxide ceramics. Barium titanate has been prepared via CVD processing of iodide precursors.[12] Recently, the preparation of $YBa_2Cu_3O_{7-\delta}$ from halide precursors including iodides was examined, and it was concluded that the iodide precursors would be preferred.[11] The following reports our studies on the use of iodide salts as solid and organic solution precursors to $YBa_2Cu_3O_{7-\delta}$.

Experimental Section

Bulk samples were fabricated from an evaporant of the iodide precursors or from a mixture of the iodides ground/homogenized in a mortar and pressed into a 13-mm-diameter by 2-mm-thick disk (SPECAC die with a Spex 35-ton press) of about 0.2 g. The solution precursors were formulated in a drybox (Vacuum Atmospheres Model HE-1) from ACS reagent grade solvents dried with 3A molecular sieves and metal iodides of 99.5% or greater purity ($BaI_2 \cdot 2H_2O$ and $YI_3 \cdot xH_2O$ from Aldrich, CuI from Cerac and Aldrich, YI_3 from Cerac). The solvent, a solution containing acetonitrile:ethanol:methoxyethanol of a composition of 60:6:5 by volume, obtained a precursor solution of about 1.4% (w/v) iodide solids. The metalloorganic solution was derived from dissolution of barium (Aldrich), yttrium isopropoxide (Cerac), and copper 2,4-pentanedionate (Aldrich) in methoxyethanol (CP grade). The resulting stoichiometric (to YBCO) solution of $Ba(OC_2H_4OMe)_2$, $Y(O\text{-}i\text{-}Pr)_3$, and $Cu(acac)_2$ was about 0.2% (w/v). Subsequently, bulk samples of the homogenized precursor were obtained by vacuum evaporation of the solution while increasing the temperature which finally approached the normal boiling point of the solvent.

Toward the close of this research a 30% solution of anhydrous metal iodides (BaI_2 from Johnson Matthey) was developed by dissolving equimolar amounts of CuI and NH_4I along with BaI_2 and YI_3 in a solvent of dimethylformamide:ethanol (2:1 ratio by volume). This was used initially for retrieving bulk samples of YBCO via vacuum evaporation and oxidation.

Two furnaces (Lindberg Models 55035 and 55322) controlled by programmable analog computers (Omega Model CN2010 and Eurotherm Model 818, respectively) were employed for thermolysis of the iodide precursors. Generally, a program commenced with a cycle in oxygen or vacuum (5 Torr of air) by ramping to 200 °C to remove excess solvent and iodine. After initial drying,

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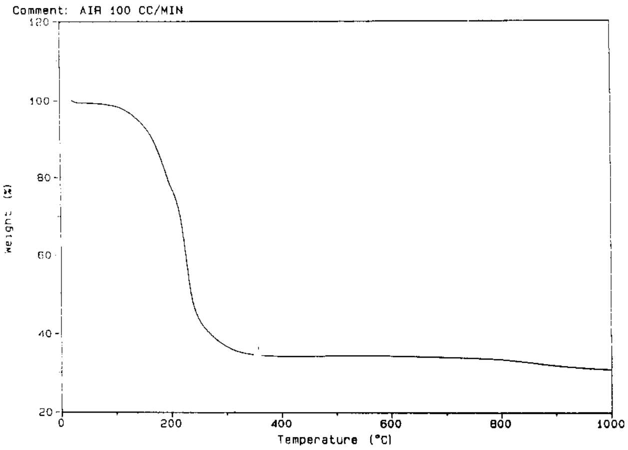

Figure 1. TGA of YI_3. Heating rate 10 °C/min.

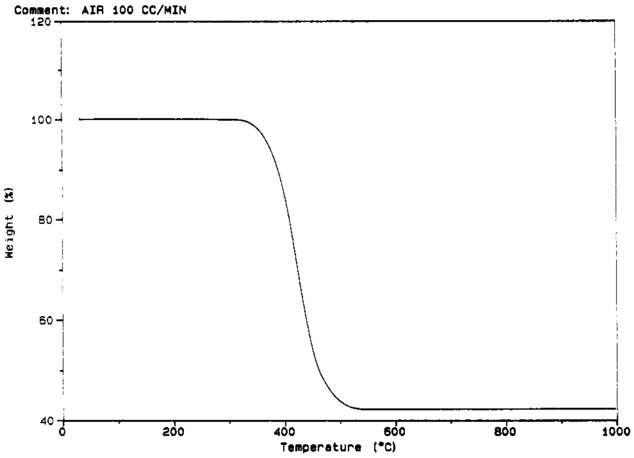

Figure 2. TGA of CuI. Heating rate 10 °C/min.

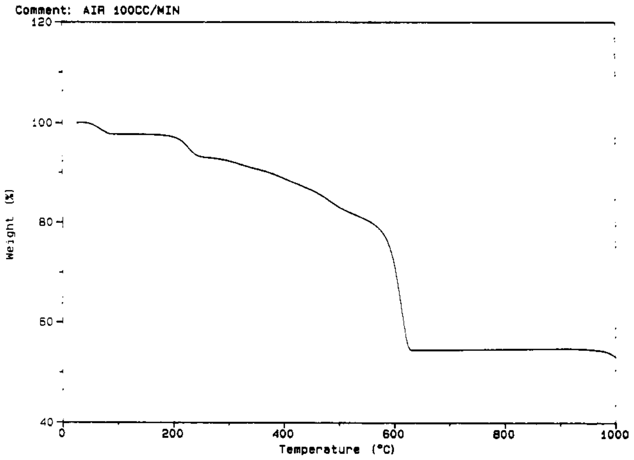

Figure 3. TGA of $BaI_2{\cdot}2H_2O$. Heating rate 10 °C/min.

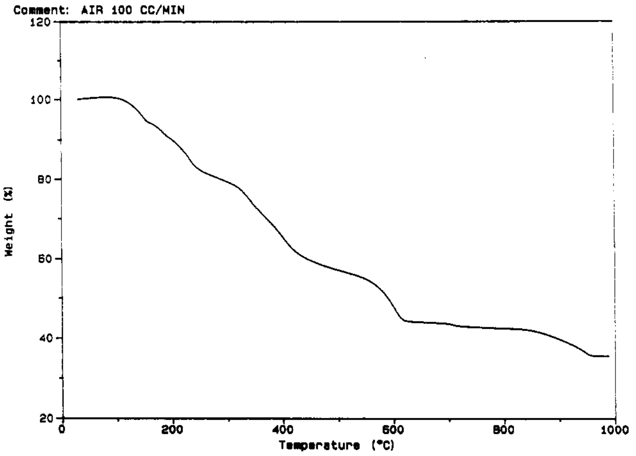

Figure 4. TGA of iodide precursor solid. Heating rate 10 °C/min.

ramp rates, soak temperatures, and times were programmed. Ambient conditions were set by means of a gas manifold in which vacuum control was monitored (CVC gauge Model GT-340A) and gas flow was controlled by rotameters into an ascarite/oil bubbler system. Ambients ranged from a few microns of air to flows of about 100 cm^3 min^{-1} of O_2, Ar, N_2, and combinations thereof. For instance, one typical cycle to produce YBCO from the iodide precursors involved ramping a pellet in oxygen to 925 °C in 40 min and soaking for 2 h at 925 °C, cooling about 1 °C/min to and holding at 450 °C for 4 h in oxygen.

The acetonitrile-based iodide solution was vacuum stripped to about a 15% (w/v) solution for spin coating (Headway Research, Inc., Model EC 101D photoresist spinner) onto $SrTiO_3$ wafers [(100) orientation from Commercial Laboratories, Inc.]. A $SrTiO_3$ wafer was spin coated at 2000 rpm 12 times, during which an air drying cycle at 200 °C was implemented between each spin. This sample was then oxidized as described above.

X-ray diffraction powder patterns were determined by a Philips Type 42271/0 diffractometer. This usually required about 10 mg of powder or about 1 cm^2 of at least a 1-μm-thick film. SEM data were collected from a JEOL Model JSM-T-300. TGA data describing oxidation and decomposition dynamics were obtained on 10-mg samples at heating rates of 10 °C min^{-1} (Du Pont Model 9900 thermogravimetric analyzer). The resistivity results were obtained at Oak Ridge National Laboratory by means of an ac "four-point" probe technique. Bulk pelleted samples were fabricated from an evaporant of the precursor solution pressed into a 13-mm diameter by 2-mm-thick disk.

Results and Discussion

TGA Studies. The decomposition of the iodide precursors to YBCO was examined by TGA in air to 1000 °C. The results are shown in Figures 1–4. YI_3 decomposes in air to Y_2O_3 at 250 °C with an expected weight loss of 76% versus the 70% found and depicted in Figure 1. This discrepancy may be due to a partial hydrolysis of YI_3 to $Y(OH)_3$. One can see in Figure 2 that CuI is fully oxidized in air at 450 °C. The weight loss of 58% is that expected for the oxidation to CuO. $BaI_2{\cdot}2H_2O$ showed loss of consecutive water molecules at 80 and 200 °C before oxidation at 650 °C, as seen in Figure 3. The water weight loss was only 6.8% compared to an expected 8.4%. This suggests partial hydrolysis of BaI_2, giving rise to the overall 47% weight loss instead of the expected value of 64%. It has been reported by Frit et al.[13] that $Ba_5(IO_6)_2$ is formed from BaI_2 in oxidative atmospheres from 200 to 400 °C and finally decomposes to BaO at temperatures exceeding 900 °C. The TGA for a mixture of the iodides gives the expected summation of the three individual curves and is shown in Figure 4.

Melting Points and Vapor Pressures of Precursor Iodides. The melting points of Y, Cu, and Ba iodides are 965, 588, and 711 °C, respectively.[14] However, the TGA studies described above show that YI_3 and CuI oxidize at 250 and 450 °C, so their melting points have no consequence in a flowing oxidative system. The TGA studies show that BaI_2 does oxidize at about 650 °C. The possibility therefore exists for melt fluxing CuO and Y_2O_3 with BaI_2 to yield YBCO in reduced oxygen ambients. The vapor pressures of BaI_2 and YI_3 are of no consequence up to 1000 °C, as they amount to about 1 mTorr here.[15,16] CuI

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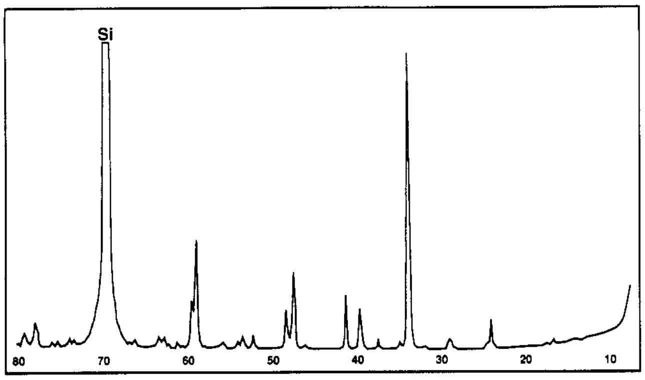

Figure 5. X-ray powder pattern of W. R. Grace $YBa_2Cu_3O_{7-\delta}$.

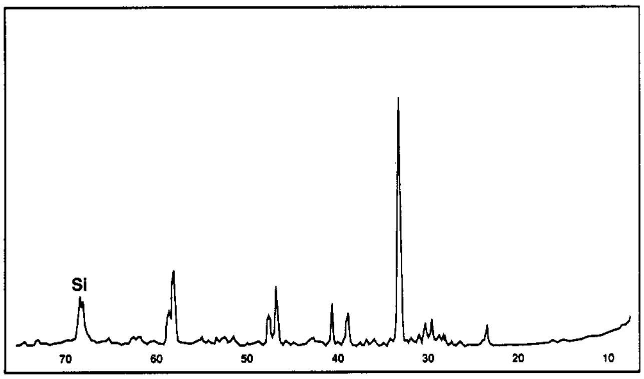

Figure 6. X-ray powder pattern of $YBa_2Cu_3O_{7-\delta}$ derived from compacted iodide powders.

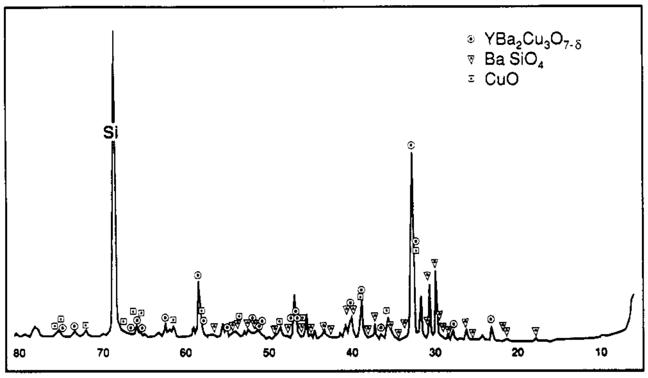

Figure 7. X-ray powder pattern of $YBa_2Cu_3O_{7-\delta}$ derived from metalloorganic solution precursor.

trimerizes to Cu_3I_3 in the vapor phase and has a pressure of 11 Torr (equivalent to 33 Torr of CuI) at 750 °C.[17] This could be a source of considerable copper losses if the CuI in the precursor is incompletely oxidized.

XRD Studies. Figures 5–9 depict the X-ray powder patterns of YBCO powders derived from a variety of sources. All samples were ramped from room temperature to 925 °C at a gross rate of 20 °C/min with delays at 450 and 650 °C to ensure oxidation of copper and barium iodides. Figure 5 is the XRD pattern ($2\theta°$) for a sample of commercial YBCO superconductor (W. R. Grace) refired in the above described schedule. This served as a standard of merit. Figure 6 is derived from a compacted powder of YI_3, $BaI_2{\cdot}2H_2O$, and CuI. This sample and the subsequently obtained monolithic powders were sintered at the solid-state reaction temperature, ground, compacted, and sintered again in the same thermal cycle. Both the homogenized oxide and iodide powders give materially the same pattern, demonstrating the feasibility of oxidizing iodide precursors to YBCO.

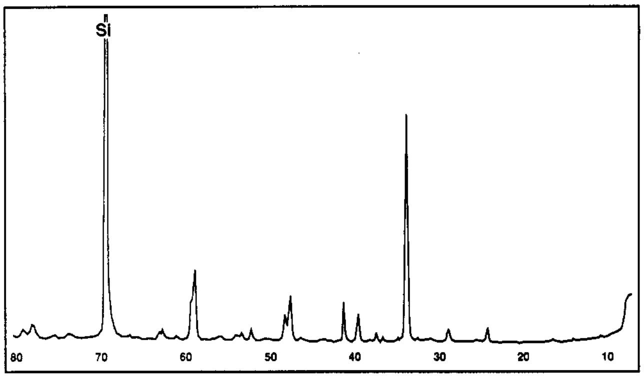

Figure 8. X-ray powder pattern of $YBa_2Cu_3O_{7-\delta}$ derived from acetonitrile solution precursor.

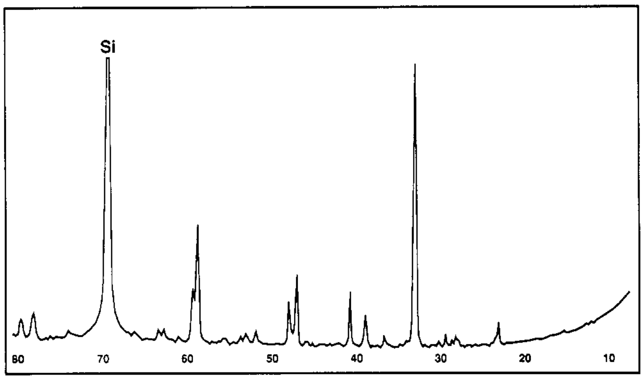

Figure 9. X-ray powder pattern of $YBa_2Cu_3O_{7-\delta}$ derived from dimethylformamide/ethanol solution precursor.

Figure 7 displays the YBCO derived from firing the evaporant of a 2-methoxyethanol solution of Y(O-*i*-Pr)$_3$, $Ba(OC_2H_4OMe)_2$, and $Cu(acac)_2$ in the same manner.[6] It is evident that the purity of this approach is not nearly as good as that from the iodide precursors. The origin of the Ba_2SiO_4 phase is not obvious, but it may arise from the low solution concentration of the method coupled with the use of glass equipment at solvent reflux temperatures, which would produce Ba_2SiO_4 in the presence of $Ba(OH)_2$. It is possible for the $Ba(OC_2H_4OMe)_2$ to react with solvent to produce $Ba(OH)_2$ and a higher molecular weight ether (a likely possibility at the boiling point of methoxyethanol, 125 °C). Trace water would allow the formation of $Ba(OH)_2$ during the formation of $Ba(OC_2H_4OMe)_2$ from Ba and methoxyethanol. Subsequent removal of solvent at temperatures approaching 150 °C to derive the solid precursor causes the formation of $BaSiO_4$ from the glassware used for the process.

In Figure 8 the XRD pattern from the metal iodides in acetonitrile shows high-purity YBCO, but the solubility of the iodides, although better than the metalloorganic system, is still only 1.4% (w/v) before concentrating (to a slurry). Finally, Figure 9 displays the XRD of the solid derived from the DMF/ethanol solvent system with 30% metal iodides in solution. Indeed, this solid shows as good purity from its solution precursor as the solid derived from powders.

The two solvent-based iodide precursors yield bulk YBCO of equivalent quality as depicted in Figures 8 and 9 with minor intensity differences related to the XRD sample thickness on the planar silicon holder. On the other hand, the quality of the bulk material derived from the metalloorganic precursor (methoxyethanol solvent) is in-

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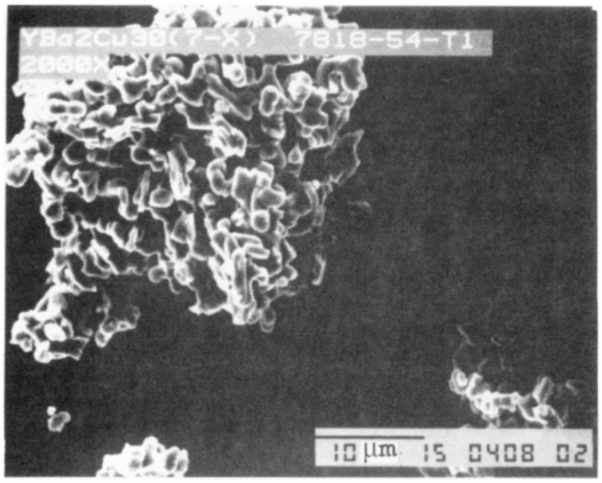

Figure 10. SEM photograph of $YBa_2Cu_3O_{7-\delta}$ derived from an iodide solution precursor.

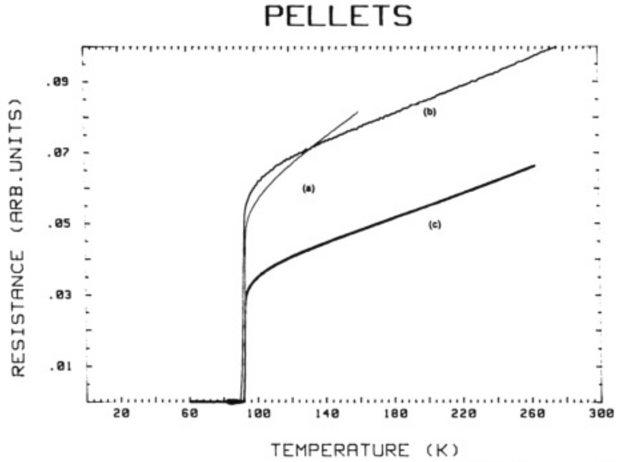

Figure 11. Resistance versus temperature for $YBa_2Cu_3O_{7-\delta}$ derived from (a) W. R. Grace powder, (b) acetonitrile-solvated iodide precursor, (c) dimethylformamide/ethanol solvate iodide precursor.

ferior for the reasons mentioned above. The solvent-based iodide precursors offer good potential for both thin- and thick-film development in a variety of processes.

SEM Studies. A portion of the YBCO powder prepared for the XRD studies from the powdered iodide precursors were examined by SEM. Figure 10 shows the micrograph of this sample. It can be seen that well-formed platelet crystals of about 5 μm are produced.

Resistivity. Figure 11 shows the resistance versus temperature measurements on a pellet of reference YBCO from W. R. Grace along with pellets made from powders prepared by vacuum drying and oxidizing solutions of the iodide precursors in acetonitrile and dimethylformamide. It is clear that the iodide precursor solution route displayed essentially the same or higher T_c of transition as the reference standard at 90 K.

Orientation on $SrTiO_3$. The acetonitrile based precursors was spin coated onto a ([100] crystal face) polished $SrTiO_3$ single crystal. To build a film thick enough to be detectable by XRD, multiple spin coatings were necessary. Figure 12 shows the XRD of a sample which had been spin coated with 12 layers and then heated in oxygen to 830 °C at 4 °C/min. After a 1-h hold at that temperature, the sample was rapidly heated to 930 °C and held for 1 h and then cooled to 450 °C and held there for 12 h. The intense reflection from the [001] axis of orthorhombic YBCO is evidence for orientation of the oxidized iodide precursor. In addition to reflections for the YBCO and the $SrTiO_3$ subtrate, several peaks for trace impurities such as CuO, $BaCuO_2$, Y_2BaCuO_5, and $Ba_5(IO_6)_2$ are observed. These impurities were generally not found in the bulk samples. Partial oxidation of BaI_2 to $Ba_5(IO_6)_2$ has been reported in the literature[13] and may result from the multiple low-temperature firing of the precursor in order to obtain enough material to be observed by XRD. The sequence of oxidative processing at low temperatures may have then promulgated other stoichimetric phases of this complex ceramic system due to the formation of $Ba_5(IO_6)_2$ and the subsequent shortage of barium.

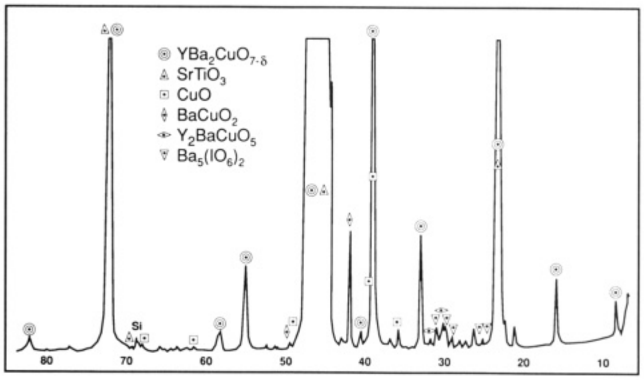

Figure 12. X-ray powder pattern of $YBa_2Cu_3O_{7-\delta}$ as a thin film on $SrTiO_3$ single-crystal derived from multiple spin coating of an iodide precursor.

Iodides Versus Other Solution Precursors. The solution precursors mentioned in the introductory discussion generally are not as soluble as the iodides with the exception of the trifluoroacetates.[9,10] Although trifluoroacetates can be dissolved in methanol up to 2 M in copper, the 0.7 M CuI solution precursor in dimethylformamide/ethanol solvent may yield more compact structures leading to similar electrical properties, if not better, in thin-film structures. The metals' density in deposited green iodide films is roughly 10 times that of the metals in a green trifluoroacetate precursor solid. This is related to the greater anionic radius and volume of the trifluoroacetate radical. A further advantage of the iodide system accrues to the lesser volatility of CuI. The volatility of CuI is not a problem until about 500 °C, while copper trifluoroacetate presents problems above 200 °C. Generally the copper oxide precursor is the most volatile component in these solution systems, but CuI is less of a problem than metalloorganic copper compounds. This latter factor allows some process leverage without concern for copper losses.

Summary

The synthesis of $YBa_2Cu_3O_{7-\delta}$ via inorganic iodide solids as well as by solutions of these solids produces materials of quality similar to that obtained from traditional oxide routes. The data presented here suggest the possibility of producing YBCO films at lower temperatures (<900 °C), in high purity, in an oriented configuration.

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Registry No. YI_3, 13470-38-7; $BaI_2{\cdot}2H_2O$, 7787-33-9; CuI, 7681-65-4.