Solution-sol-gel processing of superconductors

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Abstract. Bulk materials and thin films of pure and homogeneous $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ compounds were prepared by a nanocomposite solution-sol-gel (SSG) method. The superconducting oxides of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ were prepared at very low temperatures i.e. 750°C and 850°C , respectively by SSG method. Pellets sintered from these nanophasic sol powders showed sharp resistivity drops at $T_c \sim 90^\circ\text{K}$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $T_c \sim 67^\circ\text{K}$ for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. Thin films were prepared using triphasic sol of Y, Ba, Cu and tetraphasic sol of Bi, Sr, Ca and Cu on MgO and SrTiO_3 substrates. The triphasic sol coated on SrTiO_3 substrates and calcined at 800°C for 12 h showed the formation of superconducting phase, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with preferred orientation along the C-axis. X-ray diffraction patterns of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ films on MgO substrate showed the formation of the superconducting phase with preferential orientation along the C-axis and the microwave absorption data as a function of temperature of this film revealed the onset temperature to be 90°K .

Keywords. High temperature superconductors; sol-gel; thin film; $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$.

1. Introduction

Innovative materials processing is the key to technological utilization of the new high temperature superconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. The vast majority of syntheses of these superconductors to date involved conventional solid-state reactions of the starting materials, Y_2O_3 , CuO , Bi_2O_3 , BaCO_3 , CaCO_3 and SrCO_3 which need high temperatures and long reaction times. The key factor for the preparation of these materials at low temperatures is the synthesis of precursors through simple solution chemistry. Generating new precursors of these high T_c oxide materials through low temperature molecular chemistry is particularly important from the standpoints of powder homogeneity, purity and reproducibility. Solution routes, especially the SSG route is also ideal for low temperature processing of bulk materials, fibres, composites and coatings or thin films (Yoldas and O'keefe 1979; Dislich and Hussmann 1981; Hoffman *et al* 1984). A recent innovation of the SSG method is the utilization of heterogeneity on a nanometer scale and has been found to have profound effects on lowering the processing temperatures (Roy 1987). We have reported earlier the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ through this process at a very low temperature (Ravindranathan *et al* 1988). This paper reviews the SSG process developed in our laboratory for the preparation of both $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ in bulk as well as in thin film forms.

2. Experimental

2.1 Synthesis of bulk materials of $YBa_2Cu_3O_{7-x}$

A non-aqueous sol of copper oxide was prepared by dissolving anhydrous copper acetate, $Cu(CH_3COO)_2$ in methoxyethanol at $70^\circ C$, and refluxing the solution at $135^\circ C$ for 15–20 h. A brown solid separated out from the solution that was found to be fine-particle CuO , as confirmed by powder X-ray diffraction (XRD). Yttrium acetate was dissolved by heating in methoxyethanol at $70^\circ C$, and refluxing at $135^\circ C$ for 12 h, which resulted in a brown coloured solution, probably the ethoxide derivative of yttrium. To this solution, stoichiometric amount of barium isopropoxide was added and the mixture heated at $70^\circ C$ for a few hours. The copper sol was then added to this mixture at room temperature and stirred well. All these reactions were carried out in argon atmosphere. A slight excess of deionized water mixed with methoxyethanol in 1:4 ratio was added for hydrolysis and the mixture was refluxed for 6–10 h. The metal oxides were precipitated quantitatively from the reaction mixture by simultaneous hydrolytic decomposition of the alkoxides. The intimately mixed triphasic sol was dried at $175^\circ C$ for a few hours. The resulting gel was finely ground and calcined at various temperatures.

2.2 Preparation of thin films of $YBa_2Cu_3O_{7-x}$

Thin films of $YBa_2Cu_3O_{7-x}$ were made by dropping the above triphasic sol on the cleaned $SrTiO_3$ (hot pressed) substrate and spin casting with a speed of 2000 rpm for 30 seconds. After coating the first layer of the sol, the film was dried at $175^\circ C$ using an infrared lamp for one minute. The drying process was repeated after each coating of the sol and substrates with 10 layers were prepared to achieve sufficient film thickness. The films on the substrates were then calcined at $800^\circ C$ for 12 h and annealed in O_2 atmosphere at $500^\circ C$ for 5 h.

2.3 Synthesis of bulk materials of $Bi_2Sr_2CaCu_2O_{8+x}$

A tetraphasic sol containing Bi, Sr, Ca and Cu was prepared using bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$ (0.03 mol), strontium metal (0.03 mol), calcium metal (0.015 mol) and copper acetate (0.03 mol) and the detailed procedure is outlined in figure 1. The resulting homogeneous mixed sol can be gelled and processed into bulk materials or thin films (figure 1) of $Bi_2Sr_2CaCu_2O_{8+x}$. The gel powders calcined at $800^\circ C$ for 12 h were made into pellets and sintered at $870^\circ C$ for 12 h.

2.4 Preparation of thin films of $Bi_2Sr_2CaCu_2O_{8+x}$

The intimately mixed sols (tetraphasic) were used to make films both on $SrTiO_3$ (hot-pressed) and single crystal MgO substrates. A small amount of cladan binder was added to adjust the viscosity of these sols and the films were coated using a spin coater. The sol was spin casted on the substrate at a speed of 2000 rpm for 45 seconds. After each coating, the film was dried at $100^\circ C$. About ten layers were coated to achieve sufficient thickness and calcined at $800^\circ C$ for 6 h followed by another calcination at $870^\circ C$ for 10 minutes in air.

Figure 1. Flow chart for the preparation of bulk materials and thin films of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$.

3. Characterization

Formation of the superconducting oxide phases was confirmed by XRD. The superconducting nature of the bulk materials was confirmed by measuring the resistance of the samples as a function of temperature by the standard four-probe technique. Inductance was also measured on bulk samples to verify the superconducting behaviour. The surface morphology of the films was characterized by scanning electron microscopy (SEM). The superconducting nature of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ film on MgO substrate was confirmed by measuring the microwave absorption as a function of temperature (Jackson *et al* 1988).

4. Results and Discussion

The as-prepared triphasic gel containing yttrium, barium and copper was amorphous and the gel calcined at 800°C showed the formation of single phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. When the calcination temperature was raised to 900°C for 12 h, the phase could be indexed on an orthorhombic unit cell as reported by Wong-Ng *et al* (1987). The

advantages of this method are (a) it does not require repeated calcination and (b) a single phase can be obtained within 12 h. Others, however, reported a much longer time for calcination to achieve a single phase. The powders calcined at 800°C were made into pellets and sintered in air at 930°C for 12 h. Then the pellets were annealed at 450°C for 5 h in O₂ atmosphere. XRD of the above annealed pellet showed the formation of orthorhombic YBa₂Cu₃O_{7-x} phase. The resistance curve (figure 2) showed sharp superconducting transitions ($\sim 90^\circ\text{K}$) with widths less than 3°K from the onset to zero

Figure 2. Temperature dependence of electrical resistance for the sol-gel derived bulk YBa₂Cu₃O_{7-x}.

Figure 3. X-ray powder diffraction pattern of Bi₂Sr₂CaCu₂O_{8+x} pellet (made from powders calcined at 800°C for 12 h) sintered at 870°C for 12 h.

resistance. The inductance measurement also showed a sharp fall at the same temperature.

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film coated on SrTiO_3 substrate was calcined at 800°C for 12 h and annealed at 500°C for 5 h in O_2 atmosphere. XRD of this thin film showed the formation of the superconducting phase. The sample surface was smooth and black in colour. The thickness of the film was about $2\text{ }\mu\text{m}$. The XRD also showed that the film was preferentially oriented along the C -axis.

The tetraphasic gel powder containing Bi, Sr, Ca, Cu showed the formation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ upon calcination at 850°C for 12 h. The XRD pattern of a pellet that was sintered at 870°C for 12 h is shown in figure 3 where it can be seen that the diffraction pattern is characteristic of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ phase. The electrical resistance measured as a function of temperature showed that the onset of T_c occurred at $\sim 85^\circ\text{C}$ but zero resistance was achieved at $\sim 67^\circ\text{K}$. Scanning electron micrograph of the fracture surface of the pellet showed plate-like morphology which is typical of this superconducting phase.

The films coated on MgO and SrTiO_3 substrates using the tetraphasic sol were calcined at 800°C for 6 h and then annealed at 850°C and 870°C for 10 minutes. XRD analysis of the film annealed at 850°C indicated the presence of superconducting phase, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ semiconducting phase and some other unidentified phase whereas the film calcined at 870°C showed only the formation of superconducting and semiconducting phases. XRD pattern of the film annealed at 870°C for 10 minutes on MgO substrate is shown in figure 4. A strong preferred orientation along the C -axis of the superconducting phase was observed in the XRD pattern with the C -axis oriented normal to the plane of the film. All the $(00l)$ reflections of the film showed high intensity (figure 4). It appears that the films prepared by this method are similar to those

Figure 4. X-ray powder diffraction pattern of highly oriented thin film of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ on MgO substrate.

Figure 5. Temperature dependence of the power P reflected by $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ film on MgO substrate.

prepared by coevaporation or sputtering. The C -axis spacing observed in this film was 3.04 nm, which is slightly smaller than the 3.078 nm spacing that was determined for bulk materials (Hazen *et al* 1988). The small peaks marked with an asterisk (figure 4) may be assigned to the semiconducting phase with $C = 2.44$ nm as reported by Sunshine *et al* (1988). The microstructure of the film showed plate-like grains which was also observed by Shah *et al* (1988). It also revealed a rough surface with a grain size in the 5–8 μm range. The microwave absorption of the film was measured as a function of temperature and the plot of the power P , reflected by the sample vs temperature is shown in figure 5. It is clearly seen that the onset of superconductivity occurred at 90°K and the corresponding sharp change in the reflected power. The film coated on SrTiO_3 substrate also showed clear evidence for C -axis orientation normal to the plane of the film (figure not shown). The resistivity versus temperature measurement revealed that the T_c onset occurred at 80°K for this sample. The microstructure of this film also showed plate-like grains, as expected.

5. Summary

A nanocomposite sol-gel method has been developed for making both bulk and thin film materials of the high temperature superconductors, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. Superconducting oxides were prepared at temperatures as low as 750°C and 850°C for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$, respectively. The superconducting transition temperatures occurred at $\sim 90^\circ\text{K}$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\sim 67^\circ\text{K}$ for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. Highly oriented films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ were prepared on MgO and SrTiO_3 substrates by using this SSG route. The microwave absorption of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ film on MgO substrate showed the onset of T_c to be 90°K.

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References

- Dislich H and Hussmann E 1981 *Thin Solid Films* **77** 129
- Hazen R M, Prewitt C T and Angel R J 1988 *Phys. Rev. Lett.* **60** 1174
- Hoffman D, Roy R and Komarneni S 1984 *Mater. Lett.* **2** 245
- Jackson E M, Liao S B, Silvis J, Swihart A H, Bhagat S M, Crittenden R, Glover III R E and Manheimer M A 1988 *Physica C* **152** 125
- Ravindranathan P, Komarneni S, Bhalla A S, Roy R and Cross L E 1988 *J. Mater. Res.* **3** 810
- Roy R 1987 *Science* **238** 1664
- Shah S I, Jones G A and Subramaniam M A 1988 *Appl. Phys. Lett.* **53** 429
- Sunshine S A, Siegrist T, Schneemeyer L F, Murphy D W, Cava R J, Batlogg B, van Dover R B, Fleming R M, Glarum S H, Nakahara S, Farrow R, Krajewski J J, Zahurak S M, Waszczak S M, Marshall J H, Marsh P, Rupp Jr L W and Peck W F 1988 *Phys. Rev.* **B38** 893
- Wong-Ng W, Roth R S, Swartzendruber L J, Bennett L H, Chiang C K, Beech F and Hubbard C R 1987 *Adv. Ceram. Mater.* **2** 365
- Yoldas B E and O'keefe T W 1979 *Appl. Opt.* **18** 3133