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SYNTHESIS AND CHEMISTRY OF THE NEW Y-BASED AND BI-BASED HIGH TEMPERATURE SUPERCONDUCTING PEROVSKITES

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Abstract. — Chemical synthesis of the new high T_c oxides using solid state reactions or solution techniques is shown. A solution process which allows the preparation of both homogeneous and dense ceramics and of superconducting thick films has been developed for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system. Physical measurements performed on homogeneous $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ samples have shown that the Co substitution, associated with an uptake of oxygen, takes place on the Cu-O chains and that T_c is depressed, leading ultimately to antiferromagnetic insulators whose magnetic structures are shown. Three phases of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ with $n = 1, 2$ and 3 have been isolated in the Bi system and characterized for their structural and physical properties. These phases crystallize in the same pseudotetragonal unit cell differing one from the next by the stacking sequence along the c -axis, with the main feature being the presence of a sheared Bi-O double layer. The T_c 's of the $n = 1, 2$ and 3 phases are 10 K, 85 K and 110 K respectively, but because of phase intergrowth, these values depend upon sample processing, making chemical substitutions within the Bi system quite complex as is discussed. Finally, we succeeded in making superconducting thick films (having zero resistance around 100 K) of the Bi-based and Tl-based materials *via* the decomposition of aqueous-glycerol solutions containing the salts of the elements.

1. Introduction

Since the discovery of superconductivity at 40 K in the La-Ba-Cu-O system by Bednorz and Muller [1], much work has been devoted towards the discovery of other high T_c materials in the cuprate oxide family. This was done with the hope of enlarging this class of materials and to provide theorists with more experimental data that could help in the understanding of the origin of superconductivity in these oxides.

New materials have been found and T_c was raised from 40 K to 90 K with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase [2] whose structure contains CuO_2 planes and Cu-O chains [3]. A feature common to both the 40 K and 90 K T_c oxides is that they have closely related parent compounds that are antiferromagnetic insulators [4]. Based on these observations it was suggested that magnetism played an important role (e.g., as in the RVB model [5]) and that Cu-O chains were required to achieve the high critical temperatures. The recent discovery of superconductivity at 110 K in a Bi-based material [6] whose structure [7] does not contain chains has shown that the presence of a square planar coordinated copper (i.e. chains) is not necessary. The existence of magnetism within the Bi-based materials is still an unanswered question because of the difficulty encountered in obtaining a pure (free of second phases) insulating material, as will be discussed.

In this paper we stress material problems (namely stoichiometry and intergrowths) that exist for both the Y- and Bi-based compounds and show that homogeneous samples of $\text{YBa}_2\text{Cu}_3\text{O}_y$ can be prepared by a "sol-gel" process. A study of the $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_y$ series is presented to emphasize that reliable measurements can be obtained on homogeneous samples.

With the Bi-based materials, solid state reactions have been used to isolate the 3 phases of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ with $n = 1, 2$, and 3 and a solution technique has been developed to produce superconducting thick films of Bi and Tl cuprate oxides.

2. Y-based materials

2.1 SYNTHESIS. — The materials are usually made (solid state reaction) by heating a mixture of Y_2O_3 , CuO , and BaCO_3 or $\text{Ba}(\text{NO}_3)_2$ powders at a temperature of 950 °C for several hours and cooling slowly in an oxygen atmosphere. The resulting ceramics superconduct at 90 K, but are of low density and exhibit a low critical current J_c (500 Amp/cm²). A low J_c is usually ascribed to inhomogeneities within the sample. Solution chemistry, which allows a mixing at the molecular level, is known to produce a better ceramic. We succeeded in preparing the 123 material using solution techniques (Sol-Gel process) [8, 9]. Gels of the 123 have been obtained by mixing appropriate amounts of copper acetate, barium hydroxide and barium acetate with colloidal $\text{Y}(\text{OH})_3$ at a pH close to 7. The resulting gels can be dried to produce glassy-like materials which, after firing, give the 123 phase with a T_c of 92 K and a ΔT_c (defined as 10 % - 90 % of the resistive transition) of 0.6 K. It is important to note that, although reagent grade materials are used, this is one of the sharpest transitions measured on a bulk ceramic. The T_c is slightly lower (2 K) than that measured on solid state derived ceramics and we believe this is due to impurities in the starting reagents. For instance, the main impurity in the BaCO_3 used is strontium carbonate and we have previously shown

[10] that the substitution of Ba by Sr in the 123 material slightly depresses T_c . Impurities would also be expected to broaden the superconducting transition. The observed sharpness of the transition indicates that the impurities are evenly distributed throughout the sample (i.e. it is very homogeneous). From resistivity measurements performed on single crystals, the value of the resistivity expected for a polycrystalline dense ceramic (applying the effective medium field theory [11]) is close to that observed for our solution derived material. This implies that, using this process, we can produce a ceramic whose superconducting properties tend towards those of a single crystal. However, the critical current measured on these sol-gel derived ceramics is low and never exceeds 1000 Amp/cm².

Painting the gels on various substrates, followed by a rapid firing, produces superconducting thick films (1 to 50 microns) with T_c 's 10K lower than for the 10K lower than for the bulk (Fig. 1). One advantage of this thick film process is that we are certain of the composition and properties of the gel-derived bulk, so that, by comparison it is easier to study and control the interactions with the substrate of the gel-derived thick film.

Fig. 1. - The resistivity for a 90 % dense ceramic and the resistance of a 2 micron thick film on a MgO substrate derived from the same 123 gel, are shown as a function of the temperature. The inset shows the sharpness of the superconducting transition for the bulk ceramic.

2.2 Co-DOPED SAMPLES. - Samples of $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7-y}$ were made [12] having values of x ranging from 0 to 1. The crystal data for this Co-doped series is shown in figure 2. An orthorhombic (O) tetragonal (T) transition occurs with increasing Co content. This also is observed for Al doped samples [12], suggesting that Co is trivalent as well. Within the same range of composition the unit cell volume increases (Fig. 2b), contrary to what is expected since Co^{+3} is smaller than Cu^{+2} . The observed increase in oxygen content (determined iodometrically) upon Co doping (Fig. 2c) accounts for such an increase in the unit cell volume. Neutron experiments have shown [13]; 1) that Co is going onto the chains and adding

Fig. 2. - The lattice parameters a and b (curve a), the unit cell volume (curve b), and the oxygen content (curve c) are plotted as a function of x for the $\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7-y}$ series.

additional oxygen atoms in order to be octahedrally coordinated, and 2) that within the Ba-O planes, upon Co substitution, the barium atoms move towards the plane and the oxygen towards the chains. Thus the planes and chains become electronically isolated such that, beyond $x = 0.4$, the Co-doped samples are insulators.

In order to determine the Co valence, magnetic measurements were performed. Independent of the Co concentration, Curie-Weiss behavior was observed leading to a magnetic moment of $3.5 \mu_B$ (interval of the fit 40-300 K) per Co atom for superconducting and non-superconducting samples alike. This moment [12] does not correspond to high spin or low spin Co^{+3} . There are several possibilities which could account for the Co reduced magnetic moment including an itinerant electron contribution, a partially ordered magnetic moment or an intermediate spin configuration. In the last case one would expect to observe an anomaly (a transition from medium-spin to high-spin) in the susceptibility temperature dependence at higher temperatures. Magnetic data for oxygen deficient Co samples over the range of temperature 4.2-900 K are shown in figure 3. The Co-doped sample $x = 0.2$ follows a Curie-Weiss behavior over this temperature range, whereas an anomaly is observed around 450 K for the

Fig. 3. - The magnetic susceptibility (in a field of 7.5 kG) as a function of temperature is shown for oxygen deficient Co samples. The part of the curve indicated by an arrow is enlarged in the inset.

$x = 0.8$ Co-doped sample. Neutron diffraction data [14] have shown that this anomaly is associated with a magnetic ordering which is evidenced (on increasing the temperature) by the vanishing of the magnetic reflections $(1/2, 1/2, L)$, with L half integer only, at $T = 435$ K.

In contrast to the magnetic data, which did not show any evidence for magnetic ordering for the $x = 0.2$ Co-doped sample, neutron diffraction measurements have revealed the presence of two sets of magnetic reflections $(1/2, 1/2, L)$ with L half or whole integer) at 5 K which vanish upon increasing the temperature. The loss of the $1/2$ integer L reflections occurs at $T_{N2} = 211$ K whereas the whole integral reflections remain up to $T_{N1} = 415$ K. This contrasts with the 0.8 doped sample which shows only one magnetic transition; $T_{N1} = 435$ K for the half integral reflections. All the magnetic structures consist of magnetic Cu-O sheets with the spins lying in the plane (i.e. perpendicular to the c -axis), but differ in the stacking sequence of these planes as indicated in figure 4. To account for the intensity of the half integral reflections a magnetic moment on the Cu chain site has to be allowed, whereas such a moment is not required to fit the whole integral reflections. Note that for the $x = 0.8$ Co-doped sample, the six Cu sites fully contribute to the spin structure. This may explain why the magnetic transition is only seen by susceptibility measurements in this sample and not in the $x = 0.2$. It is interesting to recall that a magnetic ordering at $T_N = 40$ K, corresponding to half integral reflections, was recently observed for an insulating oxygen deficient 123 sample [15]. The above data shows that this magnetic ordering shifts towards higher temperatures with increasing

Fig. 4. - The orientation of the chain and plane spins is shown for each magnetic structure. Two magnetic structures are present in the $x = 0.2$ Co-doped sample, in contrast to only one for the $x = 0.8$ sample.

Co content, suggesting that there is an enhancement of the antiferromagnetic coupling between planes and chains.

3. Bi-based materials

3.1 SYNTHESIS, STRUCTURE AND PROPERTIES. - By heating (at 860°C) several mixtures containing various ratios of powdered Bi_2O_3 , CaCO_3 , SrCO_3 and CuO , we observed that the phase $\text{Bi}_4(\text{SrCa})_6\text{Cu}_4\text{O}_{16}$ is responsible for superconductivity at 85 K in the Bi system [7]. With a starting composition which contained an excess of both Bi_2O_3 and CuO , crystals were obtained and x -ray single crystal studies showed that this Bi-phase has an ideal composition $\text{Bi}_4\text{Sr}_4\text{Ca}_2\text{Cu}_4\text{O}_{16}$ and possesses a pseudotetragonal substructure, which can be viewed as a packing of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ slabs the along c -axis. The slabs are separated by $3.2 \text{ \AA}$ and shifted with respect to each other, giving this compound a layered character. Because of this lamellar character one would expect, as with other layered type materials, the occurrence of other stacking sequences, the nature of which depends upon the thermal processing (temperature, annealing time, cooling rate) used. We succeeded in isolating two other phases [16], of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ with $n = 1$ and 3, by respectively heating a nominal composition 2201 (using SrO_2 as the strontium source) in a sealed quartz ampoule at $T = 850^\circ\text{C}$, and by heating a 4334 composition close to its melting point (880°C) for several days to prepare the 2223 phase. The three Bi phases with $n = 1, 2$ and 3 were found to superconduct at 10 K, 85 K and 110 K respectively. Their structures (shown in Fig. 5) are simply related. The basis unit subcell is pseudotetragonal having the same a -axis, but with a different c -axis. The observed increase in the c -axis from $24.6 \text{ \AA}$ ($n = 1$) to $30.6 \text{ \AA}$ ($n = 2$) and $37.1 \text{ \AA}$ ($n = 3$) results from the progressive addition of 2×1 and $2 \times 2 \text{ CaCuO}_2$ slabs, each about $3 \text{ \AA}$

Fig. 5. - Crystal substructures for the Bi phases of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ with $n = 1, 2$ and 3 . The repeat unit CaCuO_2 is shown in the top left corner.

thick, to the stacking sequence in the unit cell. As with other layered-type materials we find, by means of high resolution electron microscopy (HREM), that stacking faults are common imperfections in these materials [16]. We believe that these imperfections are the origin of the wide range (10 K) of T_c 's obtained for compounds of the same nominal composition but processed differently.

3.2 CHEMICAL SUBSTITUTION. - It is well established that the non-superconducting parent compounds of the 40 K and 90 K materials are antiferromagnetic. Thus it is important to determine whether this experimental observation is still valid with the new Bi phases. Several heating processes and chemical substitutions have been tried in an attempt to reach the insulating regime without destroying the parent structure. With the $n = 1$ phase we find that materials heated at 890 °C are superconductors whereas those heated at 850 °C are semiconductors, without a noticeable change in stoichiometry. No evidence for magnetic ordering up to 400 K, as determined by magnetic measurements, was observed in the semiconducting samples. The $n = 2$ phase remains superconducting at 85 K independent of the ambient (air, oxygen, argon) used during the firing process. Thus, we have investigated the possibility of cation substitution in this phase (although this is complicated because of the possible substitution of Sr in the Ca sites and *vice versa* [7]) to achieve a semiconducting regime.

By analogy to the 40 K material ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) [17], the exchange of Sr by La within the $n = 2$ phase has been performed with the objective being a decrease in the amount of Cu^{+3} thereby generating a semiconducting-like behavior. But what we obtained, however, was a multiphase material with the $n = 1$ phase being the major phase. This indicates that a $n = 1$ phase in which Sr is replaced by La and Ca, exists as a single phase. Based on the fact that Ca and Y occupy identical crystallographic sites in both types of materials [18], the substitution of Ca by rare earths appears quite likely. We found, in accordance with the observations of others [19-20] (in studying the $\text{Bi}_4\text{Sr}_4\text{Ca}_{3-x}\text{M}_x\text{Cu}_4\text{O}_y$; $\text{M} = \text{Tm, Lu}$) that this type of substitution is successful. Figure 6 shows the results for the thulium substitution only. The samples are single phase up to $x = 2$ and multiphase for x greater than 2, so that the data are not reported for this range of composition. Upon increasing the T_m content the c -axis parameter decreases continuously whereas both the a -lattice parameter and unit cell volume (V) do not (Fig. 6a). Note that the T_m substitution produces a semiconducting material ($T_c < 4.2$ K beyond $x = 1$) and that simultaneously the oxygen content in the material increases whereas through this range of solubility the amount of Cu(III) (determined by chemical analysis [7]) remains roughly constant. This situation is similar to Co substitution in the 123 material discussed above, where Co atoms add additional oxygen atoms. Experiments are in progress to determine whether magnetic interactions exist within the insulating Bi phases.

Fig. 6. - The lattice parameters a and c (A), the unit cell volume V and critical temperature T_c (determined by the onset of the AC-susceptibility signal) (B), and the oxygen content and number of Cu(III) per total Cu (C) are shown as a function of x for the $\text{Bi}_4\text{Sr}_3\text{Ca}_{3-x}\text{Tm}_x\text{O}_y$ series.

Finally, in contrast to the 123 system, we find that the substitution for Cu by 3d metals within the 85 K phase always results in a multiphase product.

3.3 PREPARATION *via* SOLUTION TECHNIQUES. - Our synthesis studies of the 123 material indicated that solution techniques were producing better materials. With this in mind, and with the hope of preparing materials free of intergrowths, we developed a solution technique to prepare the Bi phases in a thick film form and further extended this process to prepare Tl-based materials [21]. The principle of our solution technique consists of properly complexing the Bi and Tl. The main feature of this procedure is to dissolve the Bi salt (e.g. nitrate) in a 1 to a ratio solution of water and glycerol. The salts of the other elements ($\text{Cu}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{NO}_3)_2$) are then added to the above solution to reach the desired composition (e.g. 4334). Thick films (1 to 10 microns) were

obtained either by dipping the substrate into the viscous solution or by spraying the solution onto a hot substrate. The firing process required to obtain superconducting thick films of the Bi and Tl-based materials is different because of the greater volatility of the Tl as compared to the Bi. Firing at 880 C for about 5 minutes followed by quenching is usually sufficient to obtain a 75 K superconducting Bi film. With the Tl material, an intermediate heating at 500 C is required to remove the organic component prior to a 3 minutes firing at 890 C in a sealed Pt tube containing a small amount of Tl bulk phase (to maintain the Tl vapor pressure). The T_c 's of the resulting Bi- and Tl-based films are 75 K and 105 K respectively (Fig. 7). In both systems the deposited films are highly oriented, as indicated by the X-ray diffraction patterns (Fig. 8) which show only the 001 Bragg peaks, demonstrating that the c -axis is perpendicular to the substrate. Among

Fig. 7. - Temperature dependence of the resistance for thick films of Bi-based and Tl-based cuprates. The thicknesses are 4 and 2.5 microns for the Bi and Tl films respectively.

Fig. 8. - X-ray diffraction for thallium-based thick films obtained from a glycerol solution of 2223 starting composition sprayed onto a SrTiO_3 substrate and fired at 925 °C for 5 minutes (curve A where only the phase 1223 is observed) and 2 minutes (curve B where only the 2223 phase is observed). The Bragg peaks denoted by asterisks are related to the substrate or are unidentified.

the substrates investigated (Al_2O_3 , ZrO_2 , MgO , and SrTiO_3), the best results (highest T_c and less substrate reaction) were obtained with SrTiO_3 . Depending upon the cation concentration of the starting solutions and the heating process used, single phase thick films of the 2201 and 2212 Bi-compounds, and thick films of the 2212, 2223, and 1223 Tl phases were obtained. We observe that in the Tl system the easiest phase to obtain *via* the solution technique is 1223, whereas this phase is the most difficult to obtain by solid state reaction. A possible explanation for this difference is the reaction kinetics; compound formation takes hours in the solid state process whereas it occurs within seconds when starting from solution precursors. This again confirms that solution chemistry holds promise for preparing metastable phases, having some major advantages over the solid state reaction process. However, a remaining drawback is that the superconducting films obtained have a low critical current (about 50 Amp/cm²) indicating that further work is required to fully optimize this process of interest for technological applications.

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