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Section 8: Composite materials *INVITED*

HIGH-Tc SUPERCONDUCTOR OXIDE/OXIDE COMPOSITE MATERIALS: A REVIEW AND SOME RESULTS IN THE SYSTEM «Bi-BASED HTS CUPRATES / INSULATING OXIDES»

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We present a review on superconducting composite materials. The large variety of presented couples, from metal/HTS to polymer/HST and oxide/HTS, shows the great possibilities offered by these kinds of composites.This review is focused on "oxide/oxide" superconducting composites to illustrate the potentialities of this new variety of materials. From our own results, $Bi_2Sr_3CaO_7$/Bi-2212 (or BiPb-2223) is a promising couple of oxides, which presents interesting features in view of applications for bolometers and magnetisation processes.

Keywords: Superconductor Oxides, Composite Materials, Bi-based Cuprates, HTSC

1. Introduction

Since the discovery of superconductivity in Hg by K. Onnes in 1911, the remarkable characteristic of lossless current has aroused strong interest in the field of basic physics as well as in industry. For instance, superconducting magnet technology is today in the mature stage: many large magnets for nuclear fusion experiments, superconducting magnetic resonance imaging (MRI), experimental magnetically levitated train as a future commercial transportation system. In the field of electronics, extensive studies on Josephson computers and the development of commercial superconducting quantum interference device (SQUID) systems are under way.

After the discovery of superconductive properties in barium lanthanum cuprates by Bednorz & Müller [1], the appearance in 1987 of oxide superconductors with very high critical temperature (T_c) produced great excitement in the field of basic physics as well as in practical applications, and great effort is being expended in this area. Large-scale use of high-T_c superconductor (HTS) compounds has been hindered by the fact that it is difficult to produce sizeable pieces of bulk material. For instance, high quality $YBa_2Cu_3O_{7-\delta}$ (YBCO) or $Bi_2Sr_2CaCu_2O_x$ (BSCCO) crystals rarely exceed a few mm^3 in volume [2,3]. Even when bulk ceramic samples are obtained, their mechanical fragility, poor heat conductivity and relatively high resistivity at room temperature are often insuperable obstacles to the development of reliable devices with HTS components. A simple strategy to circumvent these problems is to combine a HTS compound with another material whose role is to promote a given property in the desired way. As an example, encapsulating brittle BSCCO compounds into Ag imparts the necessary flexibility to manufactured superconductor cables [4]: this configuration is so-called a superconductor composite material.

Composite materials offer a number of benefits over more sophisticated configurations such as thin films or doped bulk materials. The main ones are their easy fabrication and a confortable control of their performances using convenient parameters. Among the composite materials, the high-T_c superconductor composites (HTSC) emerge now as an important class of materials of both academic and technologic interest with regard to different applications. Random (or granular) composites, obtained by mixing several powder materials, have attracted wide interest because of their potential use in a variety of applications [5] and in fundamental studies [6-8]. For this kind of materials, the electric conduction is well described by the percolation theory for both metal-metal and metal-superconductor composites [9,10].

In this paper, we intend to present a non exhaustive review on HTSC, with a special focus on this last category of random composites, where one of the components is a HTS oxide. Then, we will present some results obtained by our group with a particular kind of HTSC, so-called HTS "oxide/oxide" composite materials.

2. Short review on HTS composites

HTS cuprates are of four principal categories: Y-based, Bi-based, Tl-based, and Hg-based cuprates. Among them, only Y-based and Bi-based cuprates have been developed in composite configuration under several forms: wires and tapes, melt textured composites, and random (or granular) composites. Wire and tape forms are the most developed up to now because conventional superconductors – essentially bimetallic alloys (Nb-Ti) and A15 compounds (Nb_3Sn, Nb_3Al, $Nb_3(Al,Ge)$ and V_3Ga) – are manufactured under these forms from several decades and used for high field magnet applications [11] or conductor materials [12]. An important review on conventional and HTS composites under wire and tape forms, including mechanical properties, fabrication methods and engineering applications of superconductor composites, has been edited in 1994 by K. Osamura [13]. The composite configuration has been imposed with A15 compounds, which are so brittle that they are very difficult to manufacture in a large-scale production. Multifilamentary composite superconductors have been proposed to solve this problem, with the bronze processing method for the case of Nb_3Sn: Nb filaments are imbedded in the bronze matrix and the compound Nb_3Sn is formed at the interface between the Nb filament and the bronze matrix [13].

With HTS ceramic oxides, the same problems of brittleness have been solved with tentatives of composite configurations: Y-based and Bi-based cuprates under metal/superconductor wire and tape forms are essentially combined with silver for commercial and industrial applications, with good results and performances. For instance, $(BiPb)_2Sr_2Ca_2Cu_3O_x$/Ag (Bi-2223/Ag) composite has been demonstrated to be a very promising candidate for large-scale applications: values of the critical current density (J_c) of over 60 000 $A.cm^{-2}$ have been reached at 77 K for short composite tapes [14-16] and J_c values over 10 000 $A.cm^{-2}$ have been reported for long tapes over 1 000 m [17,18].

Most of these Bi-2223/Ag composites are now made by the powder-in-tube (PIT) method. Review articles on the PIT method have been presented by Dou and Liu [19] and Yamada [20]. In the PIT method, powders with a nominal composition of Bi-2223 are calcinated into a precursor powder containing mainly the $(BiPb)_2Sr_2CaCu_2O_x$ (Bi-2212) phase. The calcinated powder is filled into a pure Ag or Ag alloy tube, which is then mechanically deformed into thin composite wires or tapes. For Bi-2223/Ag composites, a thin tape is usually chosen as the final shape. The mechanical deformation process most often includes one or more of the following steps: extrusion, drawing, rolling and pressing. Basic concepts of the classical mechanical deformation theory have been applied to this process and experimental results have been recently discussed by Han et al [21] for interpreting the plastic deformation process of this kind of composites.

Random (or granular) composites are also a promising form for superconducting materials. Several combinations with HTS compounds can be envisaged, like metal/HTS, polymer/HTS, and oxide/HTS for instance. Here, we will review some couples presented in the recent literature.

Metal/HTS composites concern essentially Ag, Sn and Au metals, but also some other transition metals like Fe and Mn, and YBCO or BSCCO for HTS compounds.

Dispersion of Ag in melt grown YBCO crystals can be considered as random composites. A silver addition to Y123 is believed to be effective for the improvement of the mechanical properties without degrading the superconducting properties [22-24]. Nakamura et al have succeeded to disperse Ag particles in YBCO crystals: silver free regions are avoided if Ag_2O contents correspond to a minimal Ag concentration in the L1 (Ba-Cu rich) liquid phase of about 12.6 at% when Y123 crystals grown [25]. In Ag/YBCO granular composites, current-voltage characteristics and critical current density seem to obey an universal law and thermal conductivity is dominated by the electronic contribution of silver [26].

Gold has also been envisaged in granular composites by combination with YBCO because it does not alter its superconducting properties [27], can greatly enhance the critical current density [28], considerably improves ductibility and lowers resistivity in the normal state [29]. However, contacts between these both materials create interfaces and, sometimes, pores. The influence of porosity and secondary phases on low temperature resistivity of Au/YBCO sintered composites and the temperature dependence of their resistivity have been studied by Lambert et al [30]. A random conductor network model which incorporates porosity and interface resistances has been applied to these composites: this model is consistent with a simple picture of local modifications of the oxygen content at the YBCO-YBCO and Au-YBCO contacts [31].

Some others metals have been also combined with HTS, but without real success because a drastically oxidation of metal or attack of the superconducting parts during the sintering process: Sn/BSCCO [32,33], Fe/YBCO [34,35] and steel/BSCCO [36], Mn/YBCO [37,38], for instance.

A few composites with a polymer matrix have also been studied, like high-density polyethylene / YBCO [39], poly(phenylene sulfide) (PPS) / Bi-2223 [40], polypropylene / YBCO [41], polyester (Polymal 109) / YBCO and Teflon / YBCO [42]. In these cases, the ability of polymer matrix to protect HTS compound from moisture and other aggressive media seems the principal advantage of these couples because electrical percolation is often limited, but magnetic applications of HTS could be possible with this kind of composites. Superconducting fibers and films have been also envisaged by spinning from dispersions of HTS ceramic (YBCO and BiPb-2223) thickened with an aromatic polyamide (PABI: polyamidobenzimidazole) and subsequent firing [43].

The last series concern oxide/HTS composites, where many works have been published recently. Here, we will also account for some papers on oxide inclusions in melt textured YBCO and works on classical granular oxide/HTS composites. By using an oxide for HTS partner in composites, one can expect to limit reactivity between both phases and retain or enhance superconducting properties by the creation of flux pinning centers. In Bi-2212 superconductor, various foreign-phase inclusions have been introduced in order to improve this flux pinning. Micron-size particles of secondary phases gave rise to a several-fold J_c increase in melt-processed [44] and partially decomposed [45] ceramic samples. Substantial improvement of flux pinning was observed in Ag-sheathed Bi-2212 tape with submicron $SrZrO_3$ inclusions [46] as well as in film and bulk Bi-2212 with aligned nanorods of MgO [47]. In an addition, a processing method was developed for large shapes of Bi-2212 bulk reinforced with MgO whiskers [48,49]. MgO appeared to be a rare example of a binary oxide inert regarding to Bi-2212. A range of foreign oxide additives yielded stable phases in the Bi-2212 matrix without deterioration of the superconductivity: compatibility with Bi-2212 was established for $BaTiO_3$ [50,51], $SrZrO_3$ [52], $(Sr,Ca)In_2O_4$ [53], $(Sr,Ca)SnO_3$ [54], $Mg_{1-x}Cu_xO$ [55], $(Sr,Ca)_3Al_2O_6$ and $BiSr_{1.5}Ca_{0.5}Al_2O_z$ [56] and $Bi_2Sr_3CaO_7$ [57]. In these cases, the solubility of the additional chemical component in Bi-2212 lattice did not exceed several mol%, and T_c was not changed appreciably. With YBCO, several non superconducting oxides have been also introduced in granular composites and percolation behaviour has been studied in these materials with ferroelectric Pb_2ScTaO_6 [58,59] and insulating Ba_2GdNbO_6 [60] oxides, for instance. In the first case, strong evidence that transport in the composites takes place in 3D is shown and in the second one, the normal-state behaviour of the system matches fairly well with the theoretically expected values for an ideal metal-insulator composite system.

An alternative method to obtain superconducting materials having high critical currents is to prepare melt textured ceramics containing precipitates which create pinning centers in the bulk ceramic. In the case of YBCO ceramics, melt texturing techniques are based on the peritectic reaction occuring around 1 020°C in air, when a semisolid melt composed of solid Y_2BaCuO_5 (211) particles and a liquid with typical composition 3 $BaCuO_2$ + 2 CuO react to generate 123 crystals. Different versions of melt processing of YBCO have been investigated [61-63]. Many structural defects have been identified in 123/211 ceramic composites and their concentration and mutual interaction strongly depends on the processing methodology. Some recent progress in the understanding and improvement of directional solidification processing techniques which allow to prepare long single domain textured ceramics has been reviewed by Obradors et al [64,65]. They also described new evidences for the subtle relationship between microstructure and pinning mechanisms in these materials. These melt textured ceramics are potentially used in several technological applications, such as current leads, fault current limiters, flywheel batteries and hysteresis motors [65]. A new process has been recently proposed for the fabrication of textured RE-123/RE-211 (RE = Y, Gd) composites, vhere RE-211 preforms are infiltrated by liquid phases [66]. The major advantage of this new Infiltration and Growth (IG) method seems the facility to obtain near-net-shaped superconducting ceramics with uniformly distributed RE-211 inclusions. The process involves the fabrication of 211 preforms by conventional ceramic routes such as uniaxial and isostatic pressing, injection moulding and slip casting, and pressureless infiltration basically from a reservoir containing liquid phases. Composites containing fine and very uniformly distributed Ag is also possible by this new process.

We have studied in Marseilles some insulating oxides introduced in a Bi-based HTS cuprate matrix: obtained results with these “oxide/oxide” composites will be now briefly presented hereafter.

3. Results on «Bi-based HTS cuprate / insulating oxide» composites

Two particular kinds of non superconducting oxides have been envisaged by our group to be mixed with Bi-based HTS cuprates in order to find compatible couples of oxides able to retain the superconducting properties of the HTS oxide using it in minimal amounts. With this purpose two kinds of oxides have been selected: a first range where cations are not included in the list Bi-Pb-Sr-Ca-Cu of Bi-based cuprate cations, such as SnO_2 and InO_3, and a second one where all cations are included in this list, such as Bi_2CuO_4 and $Bi_2Sr_3CaO_7$. Bi-based HTS are either Bi-2212 (Pb-doped or not) or BiPb-2223 ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$).

All powder oxides, expected SnO_2 and InO_3 (Aldrich products) have been synthesised by classical solid state reaction techniques from carbonates or oxides. Composites are prepared by manual mixing of oxide powders, then compacted into pellets under 8 Kbar ($\varnothing$ = 13 mm; e $\approx$ 1 mm) and sintered. The sintering temperatures and durations depend on the oxide couple, after preliminary tests. Superconducting properties of the obtained composites have been evaluated only from electrical resistance measurements (ac voltage: 35 Hz) in a He closed cycle cryostat by the four probe technique between 20 and 300 K [57]. SEM observations and XRD measurements have completed the investigations. The following combinations have been investigated: SnO_2/BiPb-2223 and In_2O_3/ BiPb-2223 in the first range, Bi_2CuO_4/Bi-2212, $Bi_2Sr_3CaO_7$/Bi-2212 and $Bi_2Sr_3CaO_7$/BiPb-2223 in the second one, plus an extra oxide interesting due to its possible ferroelectric properties, $BiFeO_3$/Bi-2212 and $BiFeO_3$/BiPb-2223.

From results obtained by electrical measurements [57,67,68], we can classify these couples of oxides into two categories: i) reactive couples, when the obtained composites loose the superconducting properties even for a short sintering time (on the basis of a non null resistance response at 25 K, limit of the resistivity setup), and ii) chemically inert couples, when no detectable reactivity is observed by XRD and when the superconducting properties are kept even for a small amount of superconducting oxide (around 20-30 vol%).

Bi_2CuO_4/Bi-2212, SnO_2/BiPb-2223 and In_2O_3/BiPb-2223 belong to the first category, as the set of R(T) plots shows in the last case (Fig. 1a). Only small volume percentages are permitted in these cases to preserve superconducting properties of these composites.

In these three cases, an important chemical reaction between both oxides occurs, which is the cause of the rapid loose of superconducting properties with the formation of Bi-2201 in the case of Bi_2CuO_4/Bi-2212 [57], and of the double oxides (Sr,Ca)SnO_3 and (Sr,Ca)In_2O_4 for the other ones. We must note here the good results recently obtained by Kazin et al [53,54] when they use these double oxides in association with Bi-2212 in similar composites. They can explain the evolution of our R(T) plots with the sintering time in the case of In_2O_3/BiPb-2223 composites (Fig. 1b): the chemical reaction between In_2O_3 and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ immediately begins with the formation of the double oxide (Sr,Ca)In_2O_4. Thus the stoichiometry of the superconducting phase changes and BiPb-2212 superconducting phase is formed. The reaction stops when the entire amount of In_2O_3 has reacted, the obtained composite being now a more complicated set of BiPb-2223/BiPb-2212/(Sr,Ca)In_2O_4 composite material, with percolation possible even after 16 h of sintering at 830°C.

$Bi_2Sr_3CaO_7$/Bi-2212 and $Bi_2Sr_3CaO_7$/BiPb-2223 composites belong to the second category, as have shown our very good results already published [57,67,68]. The non superconducting oxide

$Bi_2Sr_3CaO_7$ is a copper-free phase occuring under the form of little yellow crystals during the crystal growth of Bi-2212 compound [69]. It corresponds to a solid solution studied by Rawn et al [70] and also identified under the formulae $Bi_9Sr_{11}Ca_5O_y$ by some other authors [71,72]. Its co-existence with Bi-2212 during crystal growth was a sign of its non reactivity and we have successfully tested it with the composites $Bi_2Sr_3CaO_7$/Bi-2212 [57] and $Bi_2Sr_3CaO_7$/BiPb-2223 [67]. For these composites, the most important result was the maintaining of electrical percolation even for a weak composition of superconducting phases (about 20 vol% for both oxide couples). SEM morphological studies of these materials (Fig. 2a) lead to conclude at a particular arrangement of both oxides: nodule heaps of $Bi_2Sr_3CaO_7$, about 10µm in diameter, surrounded by thin disoriented BiPb-2223 crystals, about 1 µm long and 0.1 µm thick, generally fixed in the $Bi_2Sr_3CaO_7$ grains. These small particles of BiPb-2223 are generated by manual grinding.

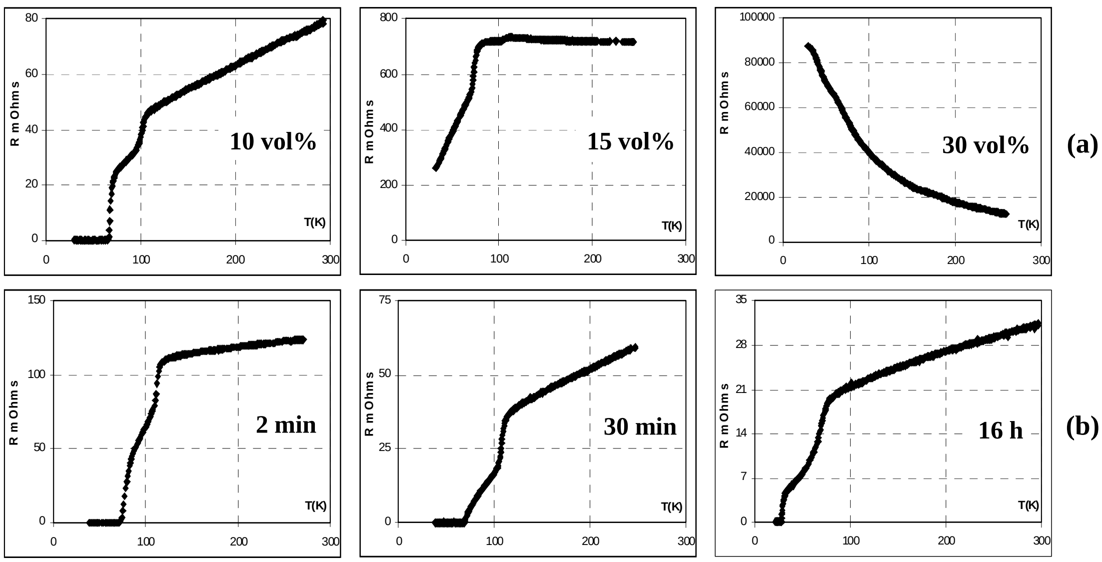

Fig. 1. R(T) plots for In_2O_3/Bi-2223 depending on the vol% of In_2O_3 ($T_{sintering}$ = 830 K; 16 hours) (a) and on the sintering duration for In_2O_3(2 vol%) ($T_{sintering}$ = 830 K) (b).

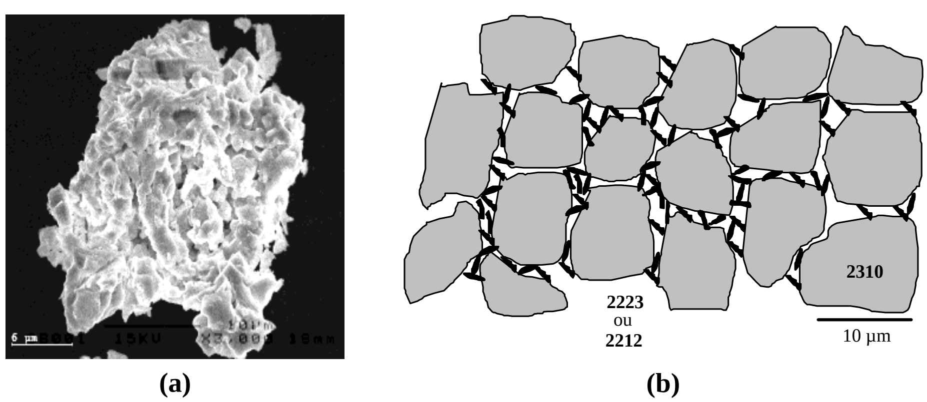

Fig. 2. SEM observations of BiPb-2223(20%)/$Bi_2Sr_3CaO_7$ composite: picture of $Bi_2Sr_3CaO_7$ nodules heap (a) and schematic representation of the 3D network (b).

This situation enables electrical percolation via the minority phase BiPb-2223 and we propose a new model of composite where percolation happens in all directions for one compound and not at all for the other, corresponding to the (3,0) symbol in the Newnham classification [73]. But in this case percolation occurs through the minority phase, so we suggest that the composite must be characterised here by $(3,0)_r$ (r for “reverse”) out of (3,0).

In such a composite, the electrical current is continuously flowing through the more or less discontinuous superconducting phase located at the surface of larger insulating grains. We are dealing with a superconducting net analogous to a 3D spider's web. Two kinds of possible applications are expected for such a superconducting net: bolometers, for wave absorption (here, the insulating oxide would play a very important role and will be part of the active composite), and magnetisation systems, with the use of a very diluted superconductive net for testing the physical properties of the neighbouring region (here, $Bi_2Sr_3CaO_7$ phase would not be active).

In this latter case, the most interesting situation would occur if we deal with an insulator sensitive to the physical properties of the neighbouring region, such as strain, electric or magnetic field (i.e., a ferroic material), which could pass the information on to the superconducting phase. For this purpose, we have also tested two new oxide couples, BiPb-2212/$BiFeO_3$ and BiPb-2223/$BiFeO_3$, where the perovskite $BiFeO_3$ is a possible candidate for interesting ferroic properties [74,75]. Studies on these last composites are in progress.

4. Conclusions

We have presented here a review on particular kinds of composite materials, where one of the components is a high-Tc superconducting phase. The large variety of presented couples, from metal/HTS to polymer/HST and oxide/HTS, shows the great possibilities offered by these kinds of composites. Up to now, applied composite materials are essentially Ag/HTS wires and tapes but Ag and oxide included in melt textured HTS materials are also a promising variety of superconducting composites.

This review is focused on "oxide/oxide" superconducting composites to illustrate the potentialities of this new variety of materials. From our own results we have selected a promising couple of oxides, $Bi_2Sr_3CaO_7$/Bi-2212 (or BiPb-2223) which presents interesting features in view of applications for bolometers and magnetisation processes.

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