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Metal–organic deposition of $YBa_2Cu_3O_x$ and $Bi_2Sr_2Ca_1Cu_2O_x$ films on various substrates starting from different fluorine-free metallorganic compounds

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Abstract. $YBa_2Cu_3O_x$ (Y-123) and $Bi_2Sr_2Ca_1Cu_2O_x$ (Bi-2212) films on various substrates have been prepared by Metal-Organic Deposition starting from different metallorganic fluorine-free compounds and using a very simple instrumentation. The processing conditions include a rapid pyrolysis step in air and an annealing step in oxygen for Y-123 and in air for Bi-2212. The films obtained have been characterized by X-ray diffraction (XRD) and the formation of a superconducting phase of Y-123 or Bi-2212 was confirmed measuring the critical temperature (T_c) with Ac-susceptibility and resistive measurements. Microstructure and final cationic ratios have been studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Keywords. Superconductors; $YBa_2Cu_3O_x$, $Bi_2Sr_2Ca_1Cu_2O_x$; metal–organic deposition; films.

1. Introduction

Films of high temperature superconductors can be obtained using different experiment procedures such as Co-Evaporation,[1–3] Sputtering,[4,5] Laser Ablation Deposition (LAD),[6] Molecular Beam Epitaxy (MBE),[7–10] Pulsed Laser Deposition (PLD)[11–13] Magnetron Sputtering,[14,15] Metal-Organic Chemical Vapour Deposition (MOCVD),[16–18] Plasma Assisted Chemical Vapour Deposition (PACVD),[19] and Sol–Gel method.[20] One of the simplest methods to obtain these films, is the Metal–Organic Deposition (MOD)[21,22] starting from a chemical solution of the precursor materials deposed on a substrate by spinning, dipping or spraying techniques. The MOD process has many advantages with respect to other preparation methods: low cost of non-vacuum processing equipments, easily controllable starting metal composition, and wide flexibility of the shape and dimension of coating object. In the last years, the MOD using trifluoroacetates (TFA)[21,23–27] as precursors has been the object of many papers and several authors have reported about the good characteristics of the obtained superconductor films. However, the TFA-MOD generally required a long pyrolysis step and/or the control of the wet N_2/O_2 ratio in the pyrolysis atmosphere moreover, highly corrosive HF gas is produced during the process. Therefore one of the aspect of interest concerning the superconductors synthesis is the development of methods with shorter annealing time and reduced or eliminated HF evolution. Cui and his co-workers report about fluorine-reduced metal-organic deposition of Y-123 films[28] obtained using copper acetate instead of copper trifluoroacetate in the starting mixture.

In this paper we report our results on of the preparation of $YBa_2Cu_3O_x$ (Y-123) and $Bi_2Sr_2Ca_1Cu_2O_x$ (Bi-2212) films obtained by MOD using fluorine-free metallorganic compounds as precursors allowing an unique and rapid pyrolysis step in air and a very simple instrumentation.

2. Experimental

The acetates, octanoates, 2-ethylesanoates, decanoates and neodecanoates of Y, Ba, Cu were used to obtain Y-123 films. Only neodecanoates of Bi, Sr, Ca, Cu were used to obtain Bi-2212 films. The

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acetates were obtained from Sigma-Aldrich, whereas all the other precursors have been synthesized following the Vest procedure.[30] To determine the real metal content a portion of each precursor was calcined and completely transformed in oxide.

Solution preparation. A mixture of xylene and pyridine was used to solubilize the precursors for Y-123, and Bi-2212. The solution viscosity plays a crucial rule in order to obtain homogeneous, uniform and crack-free pyrolyzed films. Several precursors solutions have been checked having different xylene/pyridine ratio (and hence viscosity) and the better results have been obtained using the mixture with 40 or 20% of pyridine for the syntheses of Y-123 or Bi-2212 films, respectively. Y-123 was prepared from a solution having Y : Ba : Cu 1 : 2 : 3 metal ratios and for Bi-2212 the Bi : Sr : Ca : Cu metal ratio was 2 : 2 : 1 : 2 used.

The solutions were sprayed onto metal (Ag), polycrystalline (α-Al_2O_3), and single crystal (MgO) substrates using a simple airbrush (BADGER 100-XF) connected to compressed air**.** The thermogravimetric analysis (TGA) was performed with a Du Pont 1090 instrument.

The Y-123 or Bi-2212 films synthesis is realized with a two steps heating process.

In the first step, on the basis of TGA results, after spraying, the film is heated in oven at 600°C for five minutes in air. The pyrolyzed film deposition was performed with cycles of spraying and oven heating, repeating the sequence several times: typically 20.

In figure 1 the TGA trace of the film obtained spraying the neodecanoates solution used to synthesize Y-123 samples is shown as an example. The X-ray powder diffraction spectra of the pyrolyzed samples show that $BaCO_3$, CuO, $BaCuO_2$ and $Y_2Cu_2O_5$, which are the Y-123 precursors [30], are the only compounds present in the films after pyrolysis step.

The second heat treatment step is different for Y-123 or Bi-2212: the details of the respective post-pyrolysis heat procedure are illustrated in figure 2.

Each sample was analysed with X-ray powder diffraction analysis (XRD) using a D5000-Siemens diffractometer equipped with Göbel mirrors, using Ni-filtered CuKα radiation. The diffraction intensities in 2θ-range 20°÷40° for Y-123 and 3·5°–50° for Bi-2212 were collected in a 2θ–θ scan mode, with 0·02° steps.

Samples were also investigated with a Scanning Electron Microscope (SEM) Oxford Instrument and the final cation stoichiometry was detected by EDX (Energy Dispersive X-ray) analysis.

Ac-susceptibility measurements (LakeShore7225 susceptometer) in liquid N_2 were performed on all samples in order to obtain the T_c value. The field was applied parallel to the large plane of the sample and its magnitude was 100 A/m^2 at 1000 Hz. The samples were cooled to 77K in zero magnetic field (ZFC) and the measurements were made increasing the temperature.

A home-made four probes apparatus was used for the resistive measurements.

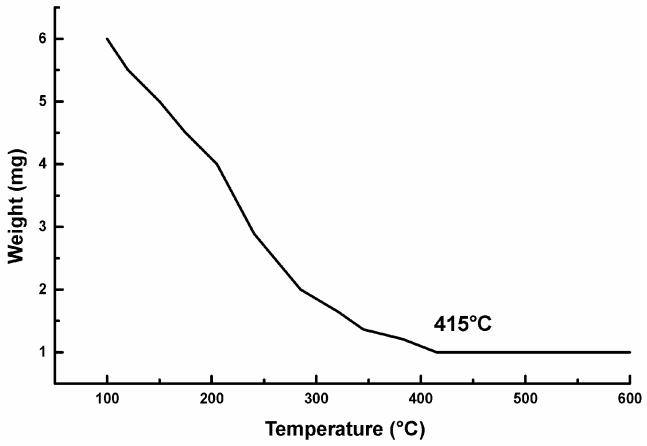


Figure 1. TGA result of the film obtained spraying the neodecanoates solution used to synthesize Y-123 samples.

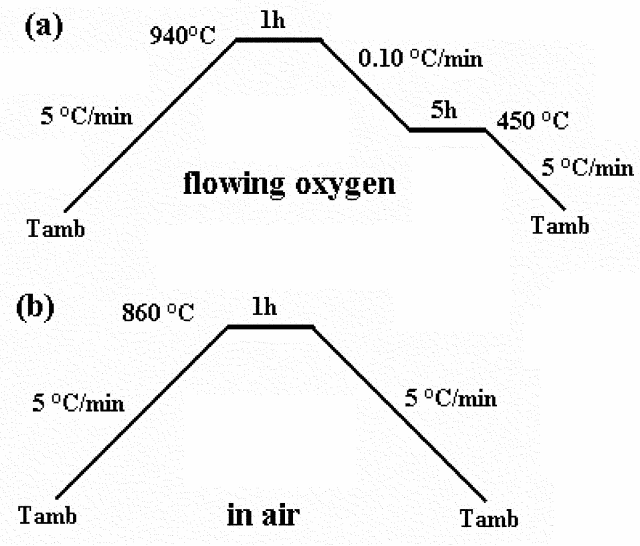


Figure 2. Second heat step procedure for YBCO (a) and BSCCO films (b).

3. Results and discussion

After the two steps heating treatment the XRD analysis has been performed of each sample and the results indicate the formation of the superconductive phase, both Y-123 and Bi-2212, on each used substrate and, for Y-123, starting from each metallorganic precursors. Films with thickness ranging from 6 to 8 μm were obtained.

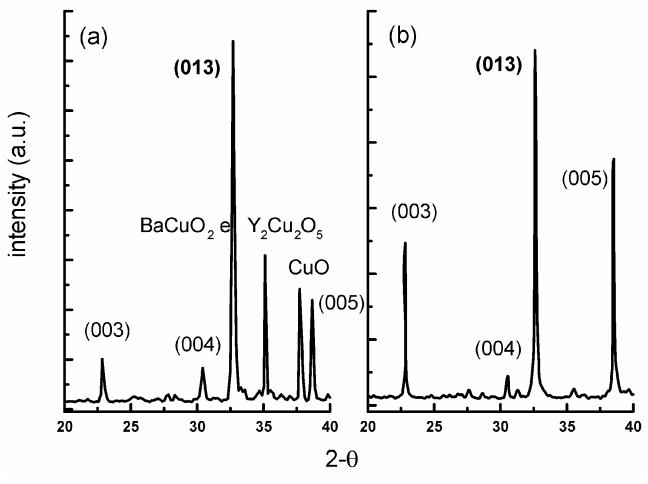
In figure 3, the XRD spectra of samples of Y-123, obtained on Al_2O_3 substrate, starting from 2-ethylesanoates and neodecanoates are reported: signals at 2θ values attributable to Y-123 phase are evident [JCPDS 38–1433]. The spectra of Y-123 synthesized using octanoates and decanoates are not shown as they are similar to those obtained from 2-ethylesanoates while, in the spectra of the samples obtained using acetates (not shown) the signals attributable to the precursors are largely predominant with respect to those attributable to Y-123 phase (even with respect to (*031*) reflection.

Moreover, the XRD patterns show that even if superconductive phase is obtained from all the precursors (except acetates), the best results are obtained using neodecanoates. In fact, in the spectra of samples obtained from octanoates, decanoates (not shown) and 2-ethylesanoates (figure 3a), signals of the precursors are still present while, the signals of superconductive phase are typical of a not-oriented (*00l*) Y-123 sample and the higher signal is that attributable to the (*031*) reflection.

If the film is synthesized using neodecanoates the peaks attributable to (*00l*) reflections clearly emerge in the XRD pattern even if the substrate (Al_2O_3) is not-oriented polycrystalline. The main signal is always due to the (*031*) reflection but its intensity, with respect to those of the (*00l*) signals, decreases. Moreover, the peaks of the precursors are suppressed (figure 3b).

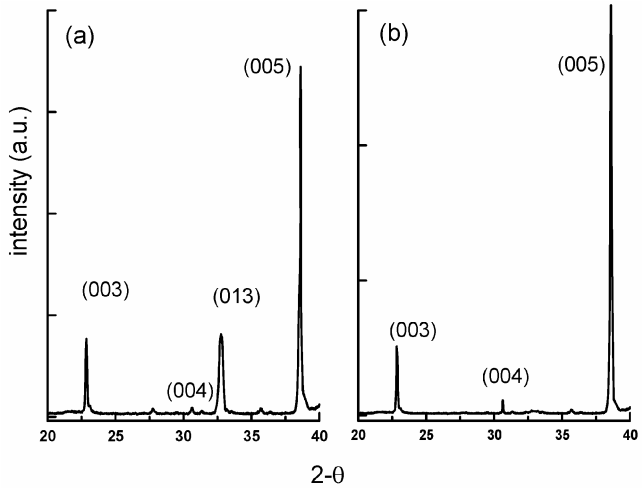
On the basis of the above results (indicating neodecanoates as the precursor leading to the best results) we have performed the Y-123 synthesis, starting from neodecanoates, on Ag and MgO to test also a metallic and a single crystal substrate. In figure 4 the XRD spectra of the films obtained are shown. From the comparison of the Y-123 samples spectra of Figures 3b, 4a and 4b, it is evident that the ratios among the peaks intensities change when Ag substitutes Al_2O_3: the (*00l*) signals increase with respect the (*hkl*) ones (particularly the (*031*) signal). As expected, this trend is more evident when MgO (monocrystalline) is used as substrate: the (*hkl*) peaks are further depressed, whereas the (*00l*) Y-123 sample orientation (and particularly the (*005*) one as substrate) is favoured.

Starting from neodecanoates we have also synthesized Bi-2212 films on Ag and MgO as substrates and in Figure 5a and b, the XRD spectra are shown. It is evident that most of the reflections and all the most intense ones are from the (*00l*) Bi-2212 family demonstrating a strong *c*-axis texture.



Note. JCPDS 38-1433.

Figure 3. XRD spectra of samples of YBCO obtained on Al_2O_3 substrate starting from 2-ethylesanoates (**a**) and neodecanoates (**b**).



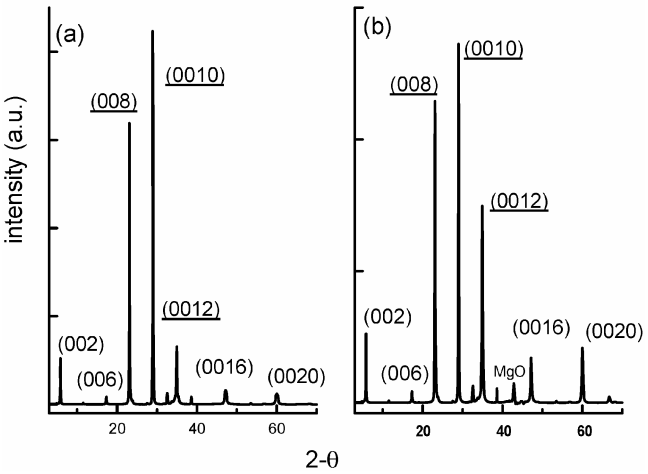
Note. JCPDS 38-1433.

Figure 4. XRD spectra of YBCO samples obtained on Ag (a) and MgO (b) substrates starting from neodecanoates.

In figure 6 the SEM picture of the Bi-2212 film obtained on MgO is shown as an example. It shows the typical oriented Bi-2212 pellet-structure.

Figure 5a and b evidences that the (*00l*) orientation of the Bi-2212 films is independent from the substrate used. However, the ratios (which are connected to the critical temperature) among the three more intense peaks (underlined in figure 5) change and the T_c value increases when MgO is used.

In figure 7 the curve of resistance vs the temperature for Bi-2212 samples obtained on MgO from neodecanoates is reported. A value of T_c (onset) around 90·2 K is observed, with a $\Delta T_c = 7$ K in agreement with the results of XRD analysis above reported.



Note. JCPDS 40-277; 41-317

Figure 5. XRD spectra of BSCCO samples obtained on Ag (a) and MgO (b) substrates starting from neodecanoates.

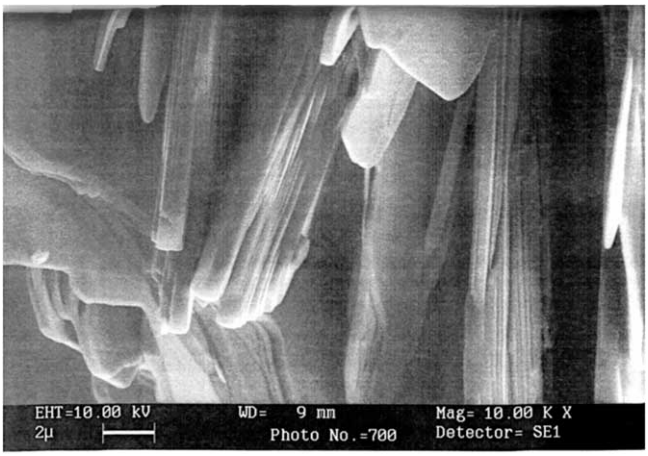


Figure 6. SEM pictures of Bi-2212 film obtained on MgO.

The samples were analysed with the EDX in order to obtain the final cation stoichiometry and values close to Y : Ba : Cu = 1 : 2 : 3, and Bi : Sr : Ca : Cu =

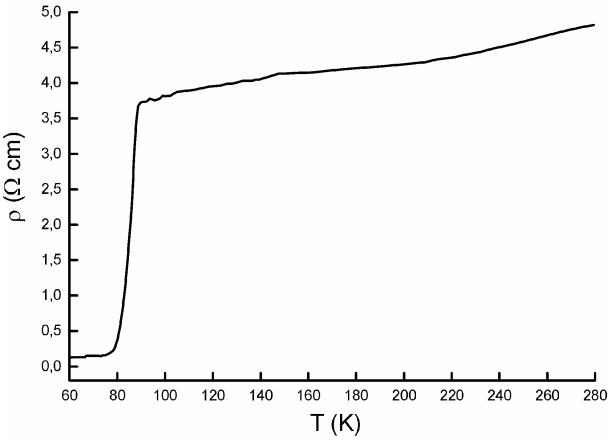


Figure 7. Curve of resistance vs. the temperature for Bi-2212 sample obtained on MgO from neodecanoates.

Table 1. Stoichiometric values of Bi-2212 and Y-123 samples obtained by EDX measurements.

Bi-2212		Y-123	
Element	Stoichiometric value	Element	Stoichiometric value
Bi	2·013	Y	1·105
Sr	2·057	Ba	2·130
Ca	0·973	Cu	3·207
Cu	1·969		

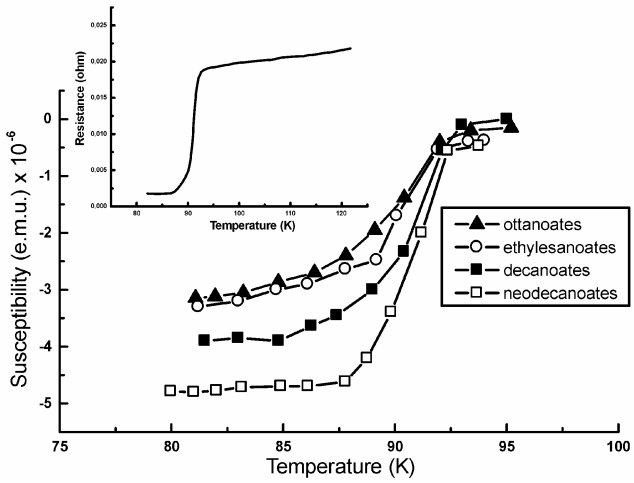


Figure 8. Change of magnetic susceptibility as a function of the temperature for YBCO films obtained on MgO substrate starting from different precursors. In the inset the curve of resistance vs the temperature for YBCO sample obtained from neodecanoates is shown.

2 : 2 : 1 : 2 for Y-123 and Bi-2212, respectively, have been obtained.

In table 1 the results of the EDX analysis on the films obtained on MgO substrate starting from neodecanoates are reported for both Y-123 and Bi-2212.

Magnetic and resistive measurements have been also performed on Y-123 films. In figure 8 the change of magnetic susceptibility as a function of the temperature is showed for Y-123 films obtained on MgO substrate, starting from different precursors. In the inset of the same figure the curve of resistance as a function of the temperature for a YBCO sample obtained from neodecanoates is also reported. The results indicate that in all the samples the superconductive phase is present and a critical temperature value (T_c) close to 92 K is observed. However, the percentage of the superconductive phase is found to depend on the precursor used, as it is evident in figure 8. With the same number of carbon atoms the quantity of the superconductive phase increases if the hydrocarbon chain is branched and, this effect is more evident if the number of carbon atoms in the precursor chain is higher.

4. Conclusions

In this paper we report on a new synthetic procedure to obtain Y-123 and Bi-2212 superconductive phases. This method shows several advantages with respect to the traditional one: (i) the pyrolysis time is shortened; (ii) the control of the wet N_2/O_2 ratio in the pyrolysis atmosphere is not necessary, as the pyrolysis step is performed in air; (iii) the highly corrosive HF gas evolution is avoided because fluorine-free precursors are used; (iiii) the experimental apparatus is very simple and not expensive.

The results obtained are very interesting as the Y-123 and Bi-2212 superconductive phases are obtainned on all the substrates used and starting from all the metallorganic precursors employed. The Y-123 and Bi-2212 films with the best superconductive properties and (*00l*) orientation are synthesized on MgO using neodecanoates.

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