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The effect of processing conditions on the properties of spray dried $Nd_1Ba_2Cu_3O_y$/Ag composite superconductors

I. Van Driessche*, B. Schoofs, E. Bruneel, S. Hoste

Ghent University Department Inorganic and Physical Chemistry, Krijgslaan 281, Bld. S3, 9000 Ghent, Belgium

Abstract

The aim of this study is to process Ag-doped $Nd_1Ba_2Cu_3O_y$ (NBCO) powders using spray drying and consequent calcinations and sintering. The influence of sintering conditions on the microstructure and superconductivity is investigated using thermal analysis (TG-DTA), X-ray diffractometry (XRD), Scanning electron microscopy (SEM), susceptibility and resistivity measurements. During sintering, a low oxygen partial pressure (1% O_2/Ar) was necessary to avoid Nd for Ba substitution. Sintering was performed at temperatures $\geqslant 990$ °C. After annealing in pure oxygen, superconducting material exhibiting Tc = 95 K was obtained. The addition of Ag whiskers led to improved grain growth and decreased intergrain contact in the superconducting phase. Negligible structural and morphological interaction between NBCO and Ag was observed.

Keywords: Composites; Oxide superconductors; Powders-chemical preparation; Superconductivity

1. Introduction

$Nd_1Ba_2Cu_3O_y$ (NBCO) has emerged as a potential alternative to $Y_1Ba_2Cu_3O_7$ superconductors, since the material exhibits both high Tc and Jc in the presence of medium range magnetic fields of 3 to 5 T.[1] The synthesis of NBCO however is extremely sensitive to processing conditions such as sintering atmosphere and temperature.[2] $Nd_1Ba_2Cu_3O_y$ usually forms $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions (Nd123ss) owing to substitution of Ba ions with Nd ions on the Ba positions. The range of solid solution is wide ($0<x<1$) and leads to a decrease in Tc of the superconducting material but can on the other hand generate high-efficiency chemical pinning centres, leading to a peak effect in the critical current density at certain magnetic fields.[3]

The increase in the ion radius for Nd^{3+} compared to Y^{3+} is also responsible for a higher geometric and thermodynamic stability of the crystal lattice and a higher peritectic decomposition temperature.[4]

Silver is a preferred doping element in superconducting materials since it significantly increases the thermal and electrical conductivity as well as the mechanical strength under low as well as under high magnetic field of the fabricated composites. Furthermore its beneficial effect on increasing critical current densities has been widely documented. Ag is also used in the fabrication of wires using the powder in tube technique and as substrate for coated conductor materials.[5,6]

The aim of this study is to process Ag-NBCO-composite powders using spray drying and subsequent calcination and sintering. The influence of sintering conditions on the microstructure and superconductivity is investigated.

2. Experimental procedure

NBCO samples were prepared from aqueous spray dried solutions of the corresponding nitrates at a concentration of 10 mass%.[7] Stoichiometric quantities of $Nd(NO_3)_3.6H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2.3H_2O$ were dissolved in distilled water to form a clear solution. The solution was atomised using a modified Buchi Spray Dryer at an inlet temperature of about 270 °C and an air stream of 800 NL/h. During this process the water from the droplets is removed thereby forming a homogeneous mixture of partially decomposed nitrates. The thermal decomposition of the precursor powders was studied using a Stanton Redcroft TG-DTA 1500 Thermobalance. The analyses were conducted in N_2 atmosphere, at a constant heating rate of 5 °C/min.

* Corresponding author. Tel.: +32-9264-44-33; fax: +32-264-49-83.

E-mail address: vandriessche@rug.ac.be (I. Van Driessche).

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The powder was subsequently calcined in air at 800 °C for 10 h, sintered at temperatures between 930 and 990 °C for 20–100 h and annealed at 400 °C in flowing oxygen. The sintering was performed in air, 10% oxygen in argon and 1% oxygen in argon atmosphere.

Ag/NBCO composites were synthesised by mixing calcined NBCO powders with Ag-whiskers in a ratio 10, 20 and 30 vol.%. The mixture was uniaxially pressed at 750 MPa and sintered using the same conditions as for the monolithic material. Ag whiskers with aspect ratio > 50 with a diameter of 20–50 μm and a length of a few hundred μm were prepared by the spontaneous electrochemical reduction of an aqueous $AgNO_3$ solution at pH 2, according to the reaction:

$$2Ag^{+} + Cu \rightarrow Cu^{2+} + 2Ag \quad E^{\circ} = 0.46V \tag{1}$$

The influence of Ag addition and of thermal conditions on the superconducting and structural features of the materials were evaluated using thermal analysis (Stanton Redcroft TG-DTA 1500), X-ray diffractometry (Siemens D5000 XRD), Scanning electron microscopy (Philips 501 SEM), AC and DC virgin magnetization by 2nd order SQUID gradiometry and resistivity measurements (Keithly 199 and N_2 flow cryostat).

3. Results and discussion

3.1. Spray dried precursor powders

Fig. 1 shows the TGA-DTA thermographs for the as-spray dried NBCO powder.

Various major weight-loss steps are apparent between room temperature and 650 °C. The total percentage weight loss at 650 °C is 45.5% which is much lower than the predicted theoretical value of 57.2% according to the following equation:

$$1Nd(NO_3)_3.6H_2O + 2Ba(NO_3)_2 + 3C_u(NO_3)_2.3H_2O \tag{2}$$

This indicates that partial dehydration and decomposition of the nitrates takes place during spray drying.

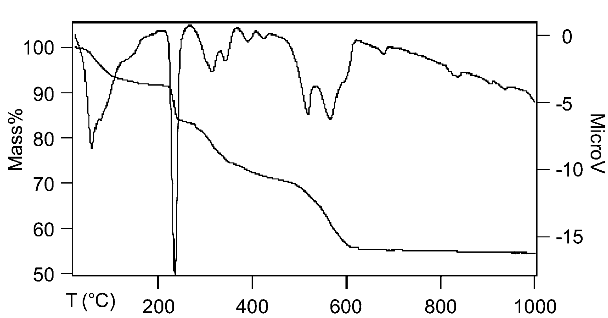

Fig. 1. TGA-DTA thermal decomposition of a spray dried $Nd_1Ba_2Cu_3O_y$ powder.

The endotherms between room temperature and 250 °C were attributed to dehydration and decomposition of Cu-nitrate to the hydroxynitrate $Cu(NO_3)_2.3Cu(OH)_2$. Between 250 and 530 °C, further decomposition of the Cu-hydroxynitrate and the Nd-nitrate takes place. The endotherm at 512 °C is attributed to the formation of Nd_2CuO_4. Between 530 and 650 °C, melting and decomposition of the $Ba(NO_3)_2$ to BaO takes place.

3.2. Thermal process

The formation of the superconducting NBCO phase and the substitution level of Ba by Nd was investigated by identification of the phases present after different sintering conditions. XRD analysis showed that after calcination at 800 °C the powder contains $BaCuO_2$ and $NdBaO_z$ mixed oxides besides the NBCO phase. At temperatures > 930 °C only the NBCO phase remains present.

Fig. 2 shows a detail of the XRD spectra for samples sintered at different temperatures and in different atmospheres. In this picture the splitting of XRD reflections for the (020/006) and (200) diffraction lines can be observed when sintering at lower oxygen partial pressure. This suggests that the tetragonal NBCO phase transforms to an orthorhombic structure, which is known to correspond to a lower level of Nd for Ba substitution.[8]

The shift of the (020/006) diffraction line to higher 2teta values when sintering at lower temperatures also indicates a phase transformation. For the orthorhombic superconducting NBCO phase, this reflection line is situated at 2teta = 46.3, as is the case for the samples sintered at 970 °C. These results show that low oxygen partial pressure and high temperature favour the formation of the orthorhombic superconducting $Nd_1Ba_2Cu_3O_7$ phase. However, susceptibility and resistivity measurements revealed that these samples showed only very poor superconducting properties.

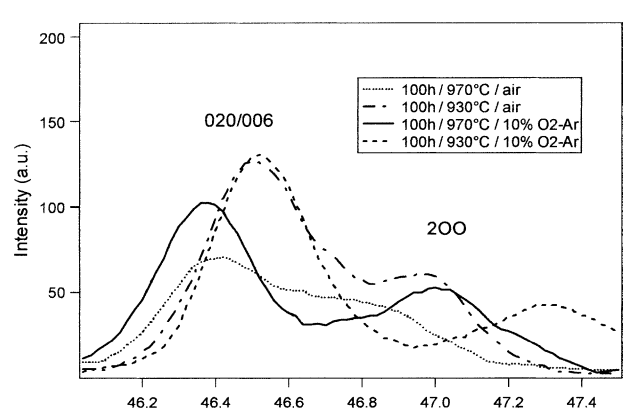

Fig. 2. Detail of the XRD diffraction lines for $Nd_1Ba_2Cu_3O_y$ samples prepared under different conditions.

Optimised superconducting samples, showing an onset Tc of 96.5 K as shown in the resistivity measurements from Fig. 3, could be obtained when sintering at 990 °C for 20h in an atmosphere with reduced oxygen partial pressure (1% O_2/Ar) and subsequent annealing for 30 h at 400 °C in pure oxygen atmosphere. Susceptibility measurements confirmed these results with an onset Tc of 95 K and a χ' value of −0.8.

3.3. NBCO/Ag composites

For samples containing more than 20 vol.% Ag, a large segregation of the metallic phase was observed after thermal treatment. These samples could not be used for further analysis. Susceptibility analysis for samples containing 10 and 20 vol.% Ag whiskers in a NBCO matrix, are shown in Fig. 4.

From this susceptibility measurement, it can be concluded that the addition of Ag has no influence on the Tc of the superconducting material.

The lower intergrain links due to the addition of Ag are shown from the smaller slope of the second step in the susceptibility curve in Fig. 4. XRD analysis revealed no formation of any secondary phase due to the addition of Ag to the NBCO matrix.

Fig. 5 shows the interface between the NBCO matrix phase (light grey) and a Ag whisker (dark grey). No alignment or ingrowth of the ceramic with the metallic phase could be observed, in contrast with previous results observed for Bi-2223/Ag superconducting composites.[9]

From EDAX analysis, summarized in Table 1, a slight migration of the metallic Ag into the ceramic matrix could be observed (point 1) as well as a migration of Ba and Cu into the metallic phase (point 4).

4. Conclusions

The present study has demonstrated that it is possible to prepare $Nd_1Ba_2Cu_3O_y$ exhibiting good superconducting properties, using spray drying and subsequent sintering under low oxygen partial pressure (1% O_2/Ar) to avoid Nd for Ba substitution. The formation rate of the orthorhombic superconducting $Nd_1Ba_2Cu_3O_7$ phase is favoured at high temperatures (>970 °C) and under low oxygen partial pressure (1%O_2/Ar). An annealing step at 400 °C in pure oxygen is necessary to obtain an optimal Tc of 96 K.

The effects of Ag addition to the $Nd_1Ba_2Cu_3O_y$ matrix were studied. Negligible structural and

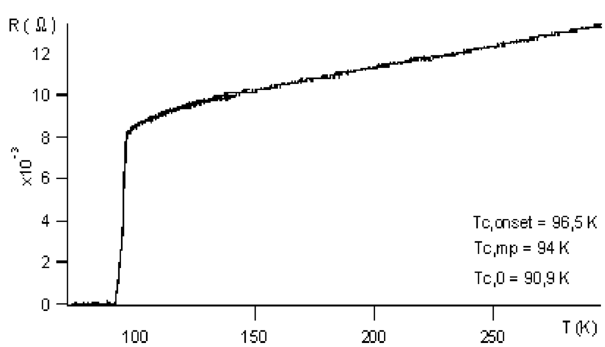

Fig. 3. Resistivity measurement for a $Nd_1Ba_2Cu_3O_y$ sample sintered at 990 °C for 20h in 1%O_2/Ar and annealed at 400 °C for 30 h in pure oxygen.

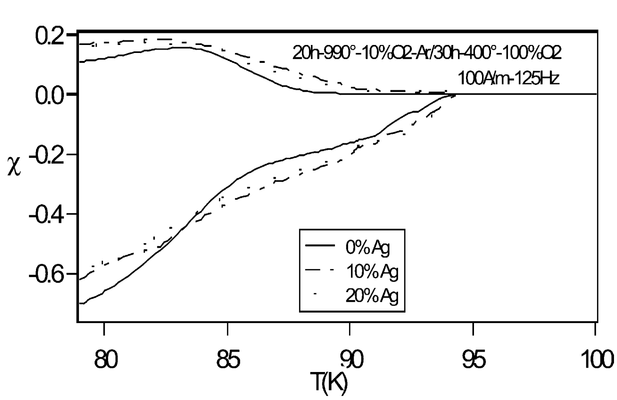

Fig. 4. Susceptibility analysis for $Nd_1Ba_2Cu_3O_y$/Ag composites.

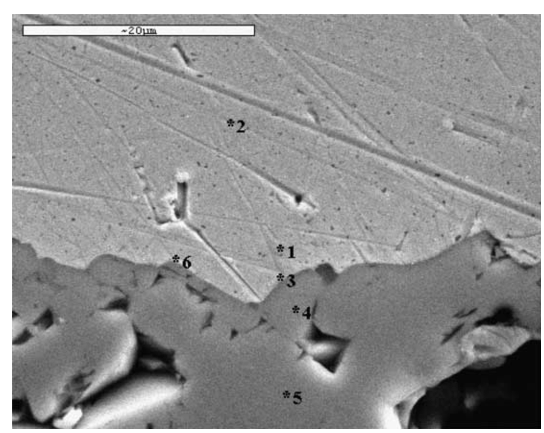

Fig. 5. SEM analysis of the interface between a $Nd_1Ba_2Cu_3O_y$ matrix and a Ag whisker.

Table 1
Atomic ratios from the SEM-EDAX analysis in Fig. 5

	% Nd	% Ba	% Cu	% Ag
Point 1	5.05	10.70	18.40	2.68
Point 2	6.24	14.34	20.66	0.49*
Point 3	1.50	3.52	6.01	25.58
Point 4	0.45*	1.38	1.96	57.00
Point 5	0.13*	0.15*	0.16*	61.27
Point 6	1.30	2.41	4.73	24.66

Percentage oxygen is not taken into account.
* $<2\sigma$

morphological interaction was shown from XRD and SEM/EDAX analysis. No texturation or ingrowth of the ceramic phase along the Ag whisker could be observed. Magnetic measurements revealed the improved grain growth and decreased intergrain contacts in the superconducting phase due to the addition of Ag.

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