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BSCCO ceramics doped with ferromagnetic manganite phases♣

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Bulk superconducting BSCCO ceramics involving a manganite phase have been obtained by two different methods: solid state synthesis and a low temperature sol-gel method. The microstructure of these materials was studied by scanning electron microscopy (SEM), X-ray diffraction and using the method of energy dispersive spectroscopy (EDX). The results suggest that the composites reveal superconductivity (at 86.6K). The obtained samples have dense structures which preserve the La-manganite phase as fine grains on the boundary with Bi phases. This composite is a potential candidate as a multifunctional material for applications in microelectronics.

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1. Introduction

The coexistence of superconductivity and ferromagnetism has attracted widespread interest associated with the critical parameters of superconductors. Maple [1] published a comprehensive review on the earlier state of this problem. Later, the studies were extended for the oxide superconductors.

As a result of experiments on mixed samples containing $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.8}Sr_{0.2}CuO_3$, in the search for a ferromagnetic-superconducting transition, the ferromagnetic compound $La_{0.8}Sr_{0.2}$ $Mn_{0.7}Cu_{0.3}O_{3+d}$ was prepared [2]. The superconductive composition $YBa_2Mn_xZn_xCu_{3-x}O_{7-d}$ with an onset temperature of 67.5K, but with a wide superconducting transition, was reported [3].

Several works have been devoted to the preparation of three-layered YBCO-$La_{0.7}Me_{0.3}$ MnO_3-YBCO materials, to optimize the epitaxial

growth in them and the interface structure of superlattices [4, 5].

The achievement T_c zero at 60 K for the $YSr_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ compound [6] and 50K in $FeSr_2YCu_2O_{7.68}$ samples [7] were pointed out. Recently, ferromagnetic superconductors in 1212 type layered cuprate $RuSr_2GdCu_2O_8$ were also discovered, with a bulk superconductivity below 46K and a Curie transition at 132 K [8-13]. A comprehensive theoretical analysis of the proximity effects in superconductor-ferromagnetic heterostructures was made by Buzdin [14]. Practically, all interesting effects related to the interplay between superconductivity (S) and magnetism (F) in S/F structures occur at the nanoscale range of the layer thicknesses.

A strong magnetic field dependence of the surface resistance can be observed in manganite/ HTS structures at $T<T_c$, due to the FMR effect [15]. Layered structures composed of oxide HTS and FM materials have attracted great attention for their importance in fundamental physics, and in potential applications in spintronics [15-19].

In our preliminary studies, superconductive behaviour below 90K and ferromagnetic properties at room

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temperature were observed in sintered bulk samples containing $La_{(1-x)}M_xMnO_3$ (M=Pb, Sr) and YBCO [20].

The above examples demonstrated the possibility of the coexistence of superconductivity and ferromagnetism in polycrystalline ceramic materials or in multilayered planar structures, but many problems arise concerning the reproducible preparation of such materials.

The purpose in this paper is to reveal the influence of the manganese ferromagnetic phase $La_{0.6}Pb_{0.4}MnO_3$ on the phase formation, microstructure and superconducting properties of BSCCO based composite bulk ceramics. This is important for the selection of an appropriate scheme for the preparation of bulk and planar superconducting doped materials with multifunctional properties.

2. Experimental

Powders of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_z$ (2223) and $La_{0.6}Pb_{0.4}MnO_3$ phases have been obtained by the Pechini method. The applied method was focused on the solution preparation technique, yielding an amorphous organic resin which can be converted to oxides by pyrolysis. It was described for the first time in a patent published in 1967 [21] on the synthesis of titanates and niobates. The process involved the dissolution of soluble salts in suitable solvents that are removed by heat treatment. A weak organic acid (citric acid) and a polyhydroxyl alcohol (ethylene glycol), allowing esterification upon heating, were used [22]. The obtained amorphous resin was heat treated and transformed into fine powdered material. The powders were mixing in the ratio 90 $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_z$:10 $La_{0.6}Pb_{0.4}MnO_3$. Following this, homogenization and pressing into pellets took place. They were heat treated at 840°C for 60 h (30 h in air and 30 h in O_2).

The samples obtained were characterized via X-ray diffraction using a Philips diffractometer (CuK_α radiation, quartz monochromator and pulse height analyzer). A computer-controlled cryostat system, giving 15 K as the lower temperature limit, was used to measure the electric conductivity by the four-electrode method.

The microstructure of the samples was studied by means of Zeiss EVO MA-15 Scanning Electron

Microscopy (SEM), with a LaB_6 cathode. Polished cross-sections from the samples were prepared. The chemical composition of the samples was determined by X-ray microanalysis, using the Energy Dispersive Spectroscopy (EDS) method -Oxford Instruments INCA Energy. The qualitative and quantitative analyses were carried out at an

accelerating voltage 20 kV, which is a normal condition for these purposes. Quantitative map (Q map) analysis was performed on 512x400 pixels for 20 hours. Optical images were taken with polarized light, using Nikon Micro hot-FX optical microscopy (OM).

3. Results and discussion

X-ray phase analysis conformed the coexistence of Bi-phases and La-manganite (Fig. 1).

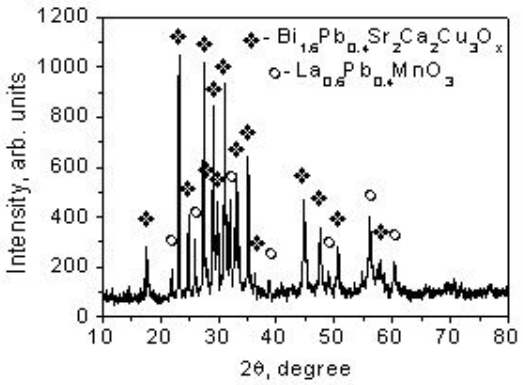

Fig. 1. X-ray patterns of the composite 90 $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_z$:10 $La_{0.6}Pb_{0.4}MnO_3$.

This study shows that the applied low temperature method is suitable for the preparation of the composites in which are preserved the initially synthesized phases. The method possesses some advantages, because the starting submicron powders can be synthesized for a short time and can be sintering at low temperature.

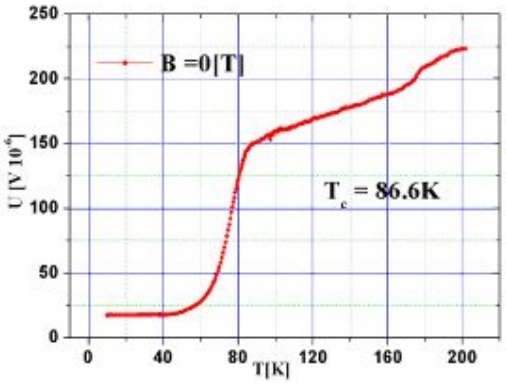

Fig. 2. U-T curve for the composite: 90 $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_z$:10 $La_{0.6}Pb_{0.4}MnO_3$.

The introduction of up to 10 $\%_{mass}$ $La_{0.6}Pb_{0.4}MnO_3$ phases did not influence significantly the superconducting properties, T_c – 86.6K (Fig. 2).

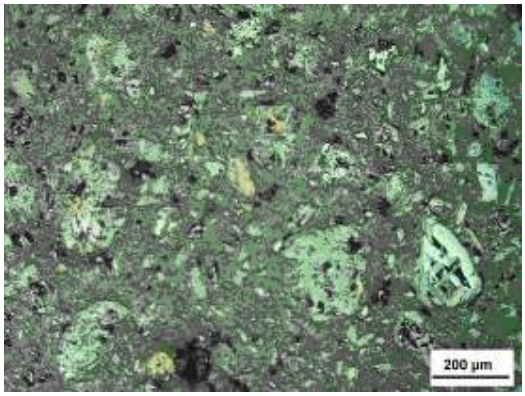

Fig. 3. Optical micrograph of the composite 90 $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_z$:10 $La_{0.6}Pb_{0.4}MnO_3$.

Several bismuthate phases and a lantanium-manganite phase have been identified by electron-probe microanalysis (Figs. 3, 4). The crystals of the main phases BSCCO are randomly distributed in the volume of the sample.

Q map backscattering electron microanalysis was used to show the distribution of different elements in a synthesized (obtained) composite (Fig. 4). One can see that light crystals (p. 1) are rich in Bi and contain little quantities of Cu and Sr. Grey crystals (p. 2) are rich in Cu, Sr and Ca. Fine crystals (p. 3) are from $La_{0.6}Pb_{0.4}MnO_3$, which is identified as an independent phase. They are situated on the boundaries of bigger crystals. The granular structure is due probably to a secondary re crystallization processes, as a result of the appearance of a liquid phase. It is evident that Cu and Pb are not uniformly distributed in large monocrystals. They show a tendency to separate into an independent phase. One can observe a good density and low porosity (lack of cavities). The reason for the superconducting transition to occur at T_c=86.6K is a result of the presence of several Bi phases after long thermal treatment.

4. Conclusions

A composite material was developed from submicron powders of La-manganite and BSCCO-ceramic, previously obtained by the Pechini method. The obtained sample had a dense structure. The La-manganite crystals were segregated on the boundaries with the Bi phases. This preliminary positive result can be used for the preparation of the many functional materials possessing superconducting and magnetic properties in different temperature ranges. Experiments for the quantitative determination of magnetic and superconducting properties are anticipated.

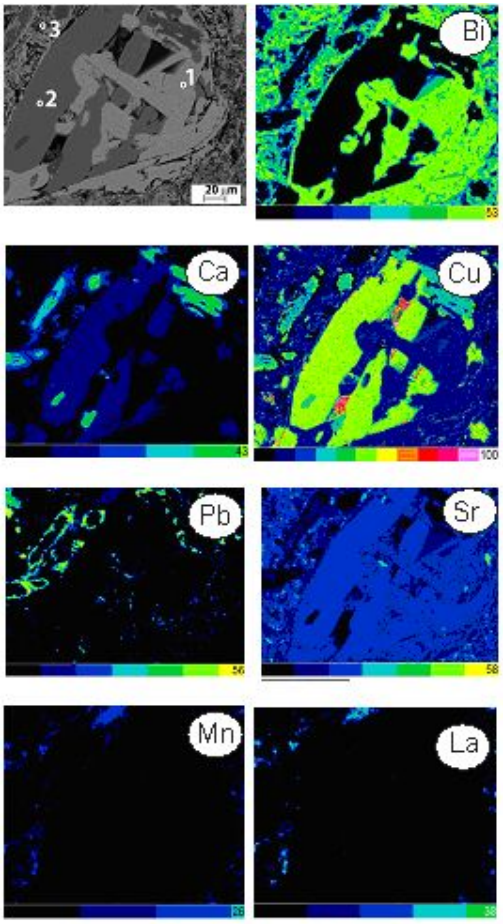

Fig. 4. Q map backscattering electron imag of the composite 90 $Bi_{1.6}Pb_{0.4}$ $Sr_2Ca_2Cu_3O_z$:10 $La_{0.6}$ $Pb_{0.4}$ MnO_3. Electron probe microanalysis images showing the composition map of different elements.

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