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# YBCO CERAMICS DOPED WITH FERROMAGNETIC $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ PHASE

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**ABSTRACT**

*Bulk superconducting composites of YBCO ($YBa_2Cu_3O_{7-\delta}$) ceramics with the participation of the magnetic $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ phase have been obtained. It was applied a solid state sintering of previous synthesized phases. Manganite additives of up to 5 $\%_{mass}$ decrease the superconducting transition temperature (Tc-onset) about to 80K and increase the critical current density (Jc) two times in relation to pure YBCO ceramics. The result of the magnetic investigations suggests that superconductivity (below 75-80K) and ferromagnetic behaviour (at room temperature) can exist in the same composite material.*

*Keywords: ceramic superconductors, YBCO, manganites, magnetic properties, composites.*

## 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 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 at 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 [4-8]. Doping of DyBCO with Zn-ions led to enhancement of the critical current density Jc [9] and in changing the behaviour of the carriers in the Bi-based superconductors [5, 10-12]. It was pointed out the achievement $T_{c\ zero}$ at 60 K for the $YSr_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ compound [13] and 50 K in $FeSr_2YCu_2O_{7,68}$ samples [14]. Recently ferromagnetic superconductors in 1212 type layered cuprate $RuSr_2GdCu_2O_8$ were also discovered with bulk superconductivity below 46 K and a Curie transition at 132 K [15-21]. A comprehensive theoretical analysis on the proximity effects in superconductor-ferromagnet heterostructures was made by Buzdin [22]. Practically all interesting effects related to the interplay between superconductivity (S) and magnetism (F) in S/F structures occur at the nanoscale range of layer thicknesses.

In our preliminary studies superconductive behaviour below 90K and ferromagnetic properties at room temperature were observed in sintered bulk samples containing $La_{(1-x)}M_xMnO_3$ (M=Pb, Sr) and YBCO [23, 24]. The above examples demonstrated the possibility of 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 is to reveal the influence of the manganese ferromagnetic phase $La_{(1-x)}M_xMnO_3$ (M=Pb, Sr) on the phase formation, microstructure, electrical and magnetic properties of YBCO-based composite ceramics. In the present study our previous studies are extended [23, 24] including a more wide range of additive compositions. The bulk composites are studed because it is possible to detect the chemical interaction during the heat treatment of the components. This is important for the selection of an appropriate scheme for preparation of bulk and planar superconducting doped materials.

## EXPERIMENTAL

The precursors $Y_2O_3$, CuO, $BaCO_3$, $La_2O_3$, $MnO_2$, $SrCO_3$ and $Pb_3O_4$ were used for the synthesis of both YBCO-ceramics and La-manganites. The YBCO phase was synthesized, following the standard ceramic technology proceeding at 930°C for 15 hours and cooling with 300°C/h in oxygen atmosphere. The manganite phase $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ was synthesized according to previous studies [25]. The batches obtained by mixing YBCO and La-manganite as an additive (0.5, 1, 2, 3, 5, 10 $\%_{mass}$) were milled and homogenized to obtain a uniform distribution of the particles. Cylindrical pellets with a diameter of 12 mm were formed by uniaxial pressing. In order to achieve a better sintering of the composites, different regimes were performed. As a result the calcinations temperature at 930°C and process duration up to 10 hours under oxygen were chosen. The samples obtained were characterized via X-ray diffraction using Philips diffractometer ($CuK_\alpha$ 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 four-electrode method. Magnetic measurements were performed by a vibrating sample magnetometer, in which the magnetic field of the sample was used for determining its magnetic moments [26]. Critical current density at a zero magnetic field was measured at 77 K using four probe contact method. The current in the circuit was determined by measuring voltage on 10 Ω standard resistor. The 10 $\mu$ V/cm voltage criterion was used for critical current definition. The microstructure of the samples was studied with Scaning electron Microscopy (JEOL Superprobe 733).

## RESULTS AND DISCUSSION

The compositions of the sintered composites and the supeconducting parameters ($T_c$-onset, $T_{co}$-zero, DT) are shown in Table 1. The introduction up to 1 $\%_{mass}$ additive did not influence significantly the superconducting properties, $T_c$ - onset is in the range 90-92K. With increasing additives amount up to 3 $\%_{mass}$, Tc decreased to 80-85K. Further increase of the manganite phase (above 3-5 $\%_{mass}$) lead to more complex R (T) curves. The samples proved to be semiconductors above Tc (onset) (Fig. 1 curves b, c). A plateau appeared on the resistance curvenear 60-80 K (Fig. 1 curve c). The superconductivity of the samples with more than 10 $\%_{mass}$ manganite phase was destroyed. The reason of this peculiarities is the increased content of the manganite additive and phase transitions in YBCO. At Fig. 2 are presented XRD paterns of the samples: YBCO, $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ and a composite material containing 97 $\%_{mass}$ YBCO + 3 $\%_{mass}$ $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$. It is difficult to distinguish the phase YBCO and

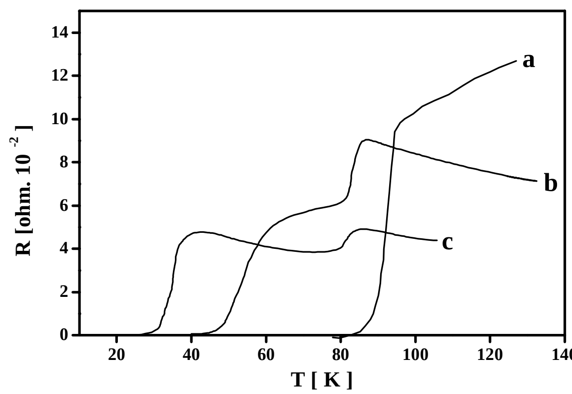


Fig. 1. R-T curves for the samples:
a - 97 $\%_{mass}$ YBCO + 3 $\%_{mass}$ $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$;
b - 95 $\%_{mass}$ YBCO+5 $\%_{mass}$ $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$;
c - 90 $\%_{mass}$ YBCO+10 $\%_{mass}$ $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$.

Table 1. Phase compositions and superconducting parameters of the composite ceramic materials.

| Composition Wt. % | Tc (onset) (K) | Tco (zero) (K) | ΔT (K) |
|---|---|---|---|
| YBCO | 92 | 91 | 1 |
| 99.5 YBCO + 0.5 $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ | 91 | 90 | 1 |
| 99 YBCO + 1 $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ | 88 | 85 | 3 |
| 98 YBCO + 2 $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ | 87 | 80 | 7 |
| 97 YBCO + 3 $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ | 85 | 78 | 7 |
| 95 YBCO + 5 $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ | 84 | 46 | 38 |
| 90 YBCO + 10 $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ | 40 | 30 | 10 |

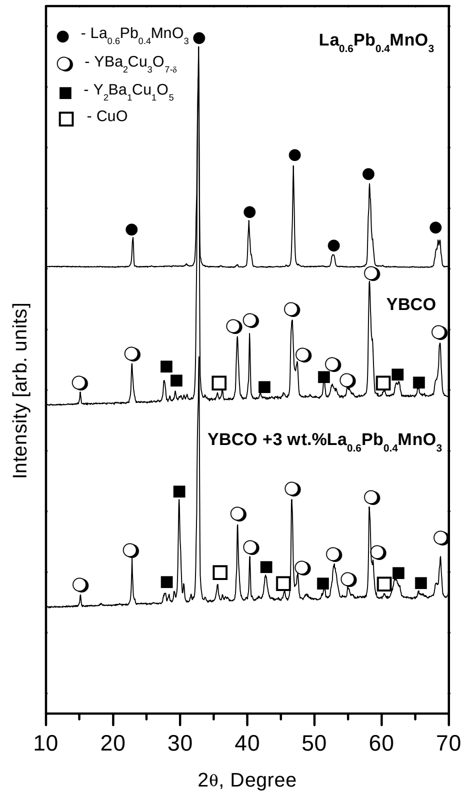


Fig. 2. XRD-patern of the samples.

$La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ due to overlapping of the strongest peaks. It was detected in the composite the presents of the phase 211 and CuO as a result of influence of the additives. More precisely several phases YBCO, $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$, $BaCuO_2$, CuO are identified by electron-probe mycroanalysis (Fig. 3). The crystals of the main phase YBCO are randomly distributed in the volume of the samples.

The critical current density (Jc) at 77 K is determined by a composite containing 5 $\%_{mass}$ $La_{0,6}Pb_{0,4}Sr_{0,2}MnO_3$.

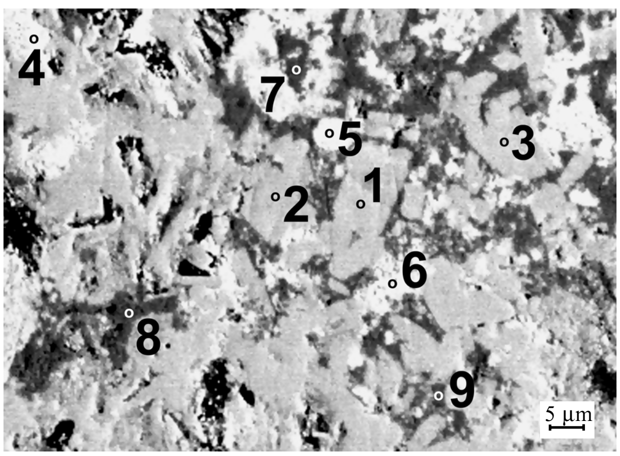


Fig. 3. Electron-probe mycroanalysis of the composite material containing 97 $\%_{mass}$ YBCO + 3 $\%_{mass}$ $La_{0,6}Pb_{0,2}$ $Sr_{0,2}MnO_3$: 1, 2, 3 - YBCO; 4, 5, 6 - $La_{0,6}Pb_{0,2}$ $Sr_{0,2}MnO_3$; 7, 8 - BaCuO2; 9 - CuO.

It is established that Jc increases up to 13,33 A/cm$^2$ while for pure YBCO ceramics Jc=7,7 A/cm$^2$). This is a positive tendency connected with the influence of the additives, but new experiments are necessary to improve the technological and electrical parameters.

Fig. 4 shows the temperature dependence of the magnetization $\sigma_s$ (emu.g$^{-1}$) in magnetic field H=2 kOe. Fig. 5 shows the magnetization as a function of the magnetic field at room temperature for the same sample. A ferromagnetic behaviour with Curie temperature $T_{Curie}$=306±5K and a value of magnetization -1,03 emu/g with saturation at 6 kOe was established. The material could be considered as a soft magnetic material with a too narrow hysteresis loop.

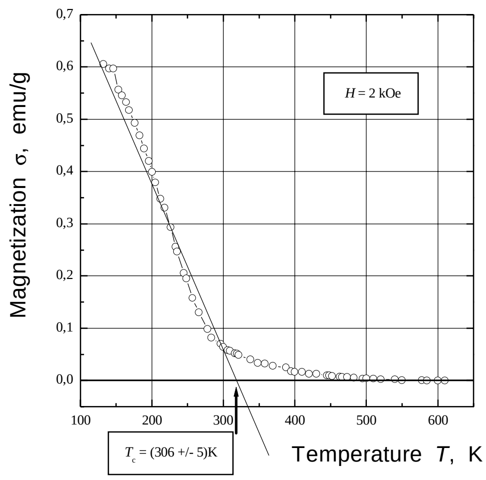


Fig. 4. Magnetization as a function of temperature of the composite material containing 97 $\%_{mass}$ YBCO + 3 $\%_{mass}$ $La_{0,6}Pb_{0,2}$ $Sr_{0,2}MnO$.

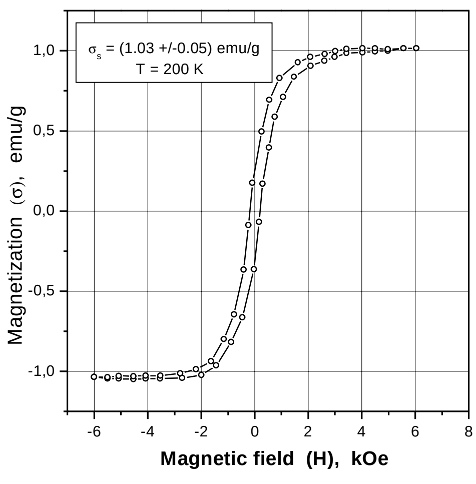


Fig. 5. Magnetization as a function of the magnetic field at room temperature of the composite material containing 97 $\%_{mass}$ YBCO + 3 $\%_{mass}$ $La_{0,6}Pb_{0,2}$ $Sr_{0,2}MnO$.

## CONCLUSIONS

It has been proved that bulk superconducting composite YBCO ceramics can be obtained with the participation of the magnetic $La_{0,6}Pb_{0,2}Sr_{0,2}MnO_3$ phase. Additives of up to 3 $\%_{mass}$ decrease the Tc to 80K but a tendency to increase the critical current density Jc was proven. The result of the magnetic investigations suggests that superconductivity (below 75-80K) and ferromagnetic behaviour (at room temperature) can exist in the same composite material.

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