Synthesis and properties of doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ superconductors

O Babych, Ya Boyko, I Gabriel, R Lutciv, M Matviyiv, B Sadovy, M Vasyuk
Electronics Department of Ivan Franko National University, Lviv, Ukraine
E-mail: orestbabych@gmail.com

Abstract. Synthesis of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (Hg-1223) with higher chemical homogeneity and large reactivity of precursor powder Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ was carried out. Pb, Fe and Cd doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ were prepared with using Hg-free precursor Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ obtained by the sol-gel method. After synthesis the samples were in the state overdoped with oxygen and reach the optimum state in flowing argon. The temperature dependences of the resistivity and magnetization measurements for different kinds of doped elements are presented.

1. Introduction
The Hg–based superconducting materials (HTSC) are compounds of the homologous series with the general composition HgBa$_2$Ca$_n$Cu$_n$O$_{2n+2+\delta}$, where $n=1,2,3$…. Among them the highest superconducting transition temperature $T_c = 133$ K was observed for $n=3$ [1]. Unfortunately, there are still problems concerning the phase stability, especially the presence of CO$_2$ and humidity. Several reports show that the phase formation and superconducting properties of Hg-1223 are enhanced by means of cation substitutions. The critical current density and phase formation of Hg-1223 can be improved at doping by high-valence type Re, Pb or other elements [2-4].

The impurities, for example Re, Pb, are catalysts for superconducting phase creating. This follows from comparison of the equilibrium mercury partial pressure temperature dependences for Hg-1223, Hg-1223 doping, and nonsuperconducting phase HgCaO$_2$, which are products of the synthesis reaction. It was shown, that the equilibrium mercury pressure for Hg,Re-1223, Hg,Pb-1223 near the HTSC synthesis temperature (860 C) is lower than that for HgCaO$_2$ what is not observed for the cleaned Hg-1223 [3].

On the other hand, creating the pinning centers with the destroying order parameter for critical current increase is necessary. Electric and magnetic states of defects play the main role in pinning vortex in superconducting materials. For example, the pinning enhancement in HTSC materials as a result of Fe ions influence on Y-, Bi- and Hg- HTSC has been shown [4,5].

At the same time, the solid state traditional synthesis process has several disadvantages such as high temperature and long time duration of synthesis. With the aim to activization of the solid state reaction the nanosized precursors were used. This leads to lowering the energy activation of Hg-HTSC phase formation.

2. Experimental
In this paper, by using the precursor method the synthesis of 15% Pb, 5% Fe and 5% Cd doped Hg-1223 was performed. The sol-gel method for preparing Pb,Fe and Cd doped precursors was used. This method has been also used for preparing nanosize powders of Y-123 ceramic [6]. Fine homogeneous and reactive Hg-free precursor Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples were obtained by the sol-gel method using acetic acid as a complex-forming agent and the acetates of Ba, Ca, Cd, Cu, Pb and Fe were used.

The synthesis from the supersaturated solution of these acetates in water-acetone solution (1:1) with ammonium citrate gel was carried out. The nanogrrelus growth in the 250-350 C range was obtained as follows:
2BaO+2CaO+2.95CuO+0.05FeO+0.15PbO= Pb_{0.15}Ba_2Ca_2Cu_{2.95}Fe_{0.05}O_{7+δ}.

This material was pressed and annealed at flowing oxygen at 900°C for 120 hours. The obtained precursor was milled along with HgO and palletized at a pressure of 75 MPa. The pellets in sealed quartz tube were heated at 860°C for 30 h and furnace was cooled down with 10°C/h. Samples of Pb, Fe and Cd doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+δ}$ superconductor were prepared by means of the following reactions (for example of Pb, Fe):

\[
0.85\text{HgO} + \text{Pb}_{0.15}\text{Ba}_2\text{Ca}_2\text{Cu}_{2.95}\text{Fe}_{0.05}\text{O}_{7+δ} = \text{Hg}_{0.85}\text{Pb}_{0.15}\text{Ba}_2\text{Ca}_2\text{Cu}_{2.95}\text{Fe}_{0.05}\text{O}_{8+δ},
\]

Microstructure of the obtained samples was observed by scanning electron microscope. Electron probe microanalysis was also carried out for determining the composition of the superconducting phase and impurity phases in the samples.

The temperature dependences of the resistivity of Pb, Fe and Cd doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+δ}$ ceramics after synthesis and annealing at 350°C for 20-50 h in flowing oxygen and argon atmosphere were measured. The superconducting transition temperature $T_c$ (on the basis of the derivative of the resistivity with temperature $d\rho/dT$) was presented. The magnetization versus temperature (4.2-140 K) and magnetic field (up to 15 kOe) measurements for different kinds of the doped elements using a Quantum Design PPMS device were carried out.

3. Results and discussion

According to the microstructure and microprobe analyses fine homogeneous Hg-free precursor was obtained (for example of Fe doping, Fig.1a).

There are three main phases in the precursor material: the grey granules of BaCu$_{1-x}$Fe$_x$O$_2$, dark granules of Ca$_2$Cu$_{1.2}$Fe$_x$O$_3$ and white granules of Ba$_3$Pb$_2$O$_5$.

Figure 1 shows the typical picture of doped Hg-1223 ceramics surface. The superconducting phase is shown in Fig.1 by the grey color. According to the microstructure analysis there are plate-like grains with a typical size of 10-20 μm. The Hg,Pb,Fe-1223 material obtained by the sol-gel method possessed high density and nonsuperconducting phases such as HgCaO$_2$ and BaCuO$_2$ were observed. The formation of HgCaO$_2$ by the interactions between HgO and oxides at 500°C was achieved, however forming Hg-1223 phase was not observed. By the microprobe analyses it has been
established that Fe is present in the superconducting phase near 5%. Probably, Fe ions replace Cu in the CuO$_2$ plane.

The temperature dependences of the resistivity of Pb, Fe and Cd doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ ceramics after synthesis and annealing in flowing oxygen and argon atmosphere for the example of Fe doping are shown in Fig.2a,b, respectively. There are two-step dependences on the superconducting transitions. The low temperature part of the transitions is very sensitive to magnetic field and depends on the intergranular media. The values of $T_c$ (determined at $d\rho/dT$ maximum) for Pb doped, Hg,Fe,Pb-1223 and Hg,Cd,Pb-1223 samples were equal to 129 K, 118 K and 126 K, respectively. After synthesis the samples were in the oxygen overdoped state and reach the optimum state in flowing argon, similarly to the case of Fe doping. From Fig.2b we can see that $T_c$ for the as-synthesized sample is equal to 118 K, while $T_c$ decreases to 113 K at annealing in oxygen and grows up to 115 K in argon atmosphere. The presence of the superconductive state for Hg,Fe,Pb-1223 sample near 77K in contrary to Pb and Cd,Pb doping is connected with an increase of the transport critical current.

The results of DC zero field cooling (ZFC) and (FC) magnetization M measurement were shown in Fig.3a. There are two-step dependences on the superconducting transitions which correlate with the electric measurements. Magnetic hysteresis loops were measured at temperature 4,2 K in applied field up to 15 kOe for different kinds of the doped elements. The intragranular critical current densities
were estimated using the Bean model [7]. These are $J_c \sim 6200 \text{ A/cm}^2$ for Hg,Pb-1223 and Hg,Cd,Pb-1223. The doping of Fe,Pb caused an increase of $J_c$ to 6800 A/cm$^2$.

4. Conclusions

Samples of 15% Pb, 5% Fe and 5% Cd doped mercury superconductor HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ were prepared employing highly homogeneous and reactive Hg-free precursor Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ obtained by the sol-gel method. According to microstructure and microprobe analyses the fine homogeneous Hg-free precursor was obtained. On the basis of the temperature dependences of the resistivity of doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ ceramics (for the example of Fe doping) it was shown that after synthesis the samples were in oxygen overdoped state and reach the optimum oxygen content in flowing argon.

Measurements of the magnetization versus temperature (4.2-140K) and magnetic field (to 15 kOe) for different kinds of doped elements were performed. The Fe doping of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples shows decreasing T$_c$ however gives rise to pinning enhancement of the material and increasing the critical current.

References

[1] Schilling A, Cantoni M, Guo J D and Ott H R 1993 Superconductivity above 130K in the Hg-Ba-Ca-Cu-O system. Nature 363 56-58
[2] Passos C A C, Orlando M T D, Oliveira F D C, da Cruz P C M, Passamai Jr J L, Orlando C G P, Eloï N A, Correa H P S and Martinez L G 2002 Effect of oxygen content on the properties of the Hg$_0.18$Re$_{0.18}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ superconductors. Supercond. Sci. Technol. 15 1177-1183
[3] Knizek K, Veverka M V, Pollert E, Sedmidubsky D and Bryntse I 2002 Mercury pressure during synthesis of the HgBa$_2$CaCu$_2$O$_{6+\delta}$ superconductor. Physica C 371 N. 2 111–116
[4] Tian W, Shao H M, Zhu J S and Wang Y N 2006 Depinning lines of Fe- and Pb-doped High-T$_c$ superconductors HgBa$_2$Ca$_2$Cu$_3$O$_{6+\delta}$ Physica Status Solidi (b) 196 373-378
[5] Togulev P N, Bazarov V V, Khaibullin I B and Suleimanov N M 2002 Reinforcement of pinning by surface magnetic microparticles in high-Tc superconductors. Low Temp. Phys. 28 250-253
[6] Levytska K E, Voitenko T A and Nedilko S A 2007 Superconductivity in Y$_x$YBa$_2$$_7$-5$_{Cu}_3$O$_{8+\delta}$ system. Physica C 460-462 722-723
[7] Bean C P 1962 Magnetization of hard superconductors. Phys. Rev. Lett 8 250-253