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The preparation and magnetic properties of the high T_c-superconductor (2234) $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$

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Abstract

The processes of phase formation and magnetic properties of the high T_c Bismuth system with four (n=4) CuO_2 - layers has been investigated.

1.Introduction

Bi-based materials become promising candidates for the fabrication of superconducting wires and tapes.The very important purpose is to prepare superconducting materials with higher critical parameters (lower critical field H_{c1}, upper field H_{c2}, current density J_c, critical temperature T_c).

In fact, in the system Bi-Sr-Ca-Cu-O exist three various superconducting phases with different contents of Ca and Cu, generally expressed by the form $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (where n is the number of CuO_2 layers in the unit cell). There are phases 2201 (n=1), 2212 (n=2) and 2223 (n=3) with different critical temperatures 10, 80 and 110 K [1], respectively.

The superconducting phases with very high critical temperatures exist in system $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ for $n \geq 4$ CuO_2 - layers. This was confirmed also by model calculation in [2]. The authors Eab. Chai et al. [2] prepared HTSC $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2+x}O_y$ (x=0.8-1.0; T_c=140 K,T_c(R=0)≅ 117K). The formation of 2234 phase with T_c=140 K was supposed in $BiSrCaCu_2O_x$ [3]. The 2235 phase (c=48 Å, T_c=180 K) is characterized as structuraly instable in bismuth system [4,5]. We obtained the high T_c- superconductor $(Bi,Pb)_2Sr_2Ca_3Cu_4O_y$ (T_c≅ 107 K) [6] by very long annealing in temperature range 870 - 880 °C in the system Bi-Pb-Sr-Ca-Cu-O. We found no correlation of the number of CuO_2 layers and parameters such as H_{c1},H_{c2}, and J_c for n≥4 HTSC bismuth system in literature. It is known that excess of Ca_2CuO_3 in $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Cu_3O_y$ [6] follows increasing critical parameters the temperature T_c, the fields H_{c1},H_{c2}, and the critical current density J_c. The$[Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Cu_3O_y]_{1-x}$-$[Ca_2CuO_3]_x$ system can be considered as HTSC with n>3 because $n_{Cu}=3+x>3$ and $n_{Ca}=2+2*x>2$. The aim of our work is to study the formation of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ phase and its superconducting properties.

2.Experimental

The samples were characterized by X-ray powder diffraction, thermography, electron microscopy, metallography, X-ray spectroscopy and by magnetic measurements. The samples were prepared by melt sintering method and by original many steps technology from Bi_2O_3, PbO, CuO, $Ca(NO_3)_2$ and $Sr(NO_3)_2$.

The synthesis temperature T_1,the sintering temperature T_2 and the annealing time τ were changed in range $T_1 \in (780-820)$ °C,$T_2 \in (835-850)$ °C and $\tau \in$ (30-100) hours. Magnetic measurements were carried out in temperature range

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4.2-150 K using a set-up based on the Faraday method (Oxford Instruments Susceptibility System) and AC susceptibility. We have measured hysteresis loops at various temperatures and temperature dependencies of susceptibility in fields up to 0.4 T. The X-ray patterns were recorded at room temperature using a X-ray diffractometer HZG4 (Cu-K_α radiation).

3.Results and Discussion

The X-ray phase analyses of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ samples proved three polymorphous modifications of 2234 phase:
α-F centred pseudo-rhombic cell with parameters a_α=5.32 Å, b_α=5.42 Å, c_α=37.1 Å, γ_α=90° ; β - B centred monoclinic cell where a_β=5,32 Å, b_β=3.82 Å, c_β=37.1 Å, γ_β=135° ; γ-I centred monoclinic cell with parameters a_γ=3.779 Å, b_γ=3.834 Å, c_γ=37.15 Å, γ_γ=90° 15'(monoclinic system I112) [7]. The investigated samples consist of α, β, γ modifications of phase 2234 and unknown X-phase with C_α=60, C_β=9, C_γ=20, C_x=11, $C_{\alpha+\beta+\gamma}$=89 (contents in per cent were determined by the X-ray diffraction).The $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ samples consist of thin flatted grains with 6-15μm diameter, 0.25-1μm height.

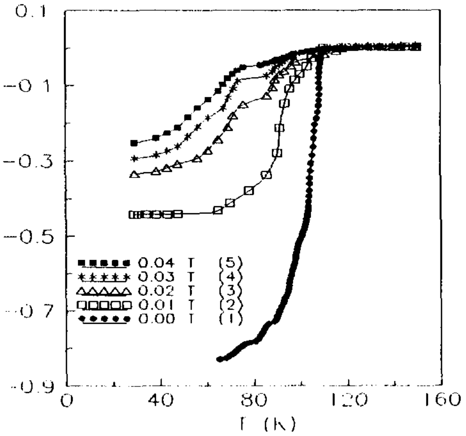

Fig.1

The temperature dependencies of susceptibility of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ in field (1) 0 T; (2) 0.01 T; (3) 0.02 T; (4) 0.03 T; (5) 0.04 T, respectively.

The monoclinic γ-modification of phase 2234 has characteristic octagonal bounds with average side 0.75-1μm. From our point of view the X-phase ($T_c \approx$65 K) competented to the insufficient 2212 phase with contents $Bi_{2-x}Sr_{2+x}Ca_{1+x}Cu_{1.5-1.6}O_y$ and parameters a=b≈5.42 Å, c≈27.65-28.3 Å (pseudo-tetragonal system).

The temperature dependencies of magnetic susceptibility in HTSC 2234 are shown in Fig.1. The typical sharp superconducting transition with $T_c^{onset} \approx$ 108 K in the temperature dependence of AC - susceptibility in the weak field represent curve 1 (Fig.1). The magnetic susceptibility reaches the value 0.82 of full Meissner effect with decreasing temperature to 70 K. Increasing external field extends the superconducting transition (B≤ 10 mT, curve 2) and then at T ≤70 K, B≥ 20 mT follows to superconducting transition of second phase with $T_c^{onset} \approx$ 65 K (curve 3, 4). The creation of "65 K phase" in weak field in HTSC was achieved by a last annealing at the temperatures higher than 865° C or by oxofluorid doping. From our point of view the "65 K phase"in samples $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ in the magnetic field is combined by weak Josephson coupling between high $T_c \approx$107 K grains. The weak Josephson coupling weakens a shielding effect of sample volume [8]. The shielding efficiency is determined by the critical current of Josephson's contact of SC-grains. The critical current of SC grains is much higher than critical current of Josephson's contacts. The Josephson's shielding decreases with increasing of magnetic induction B,it means that content of "Josephson's phase" decrease with increasing of magnetic field.

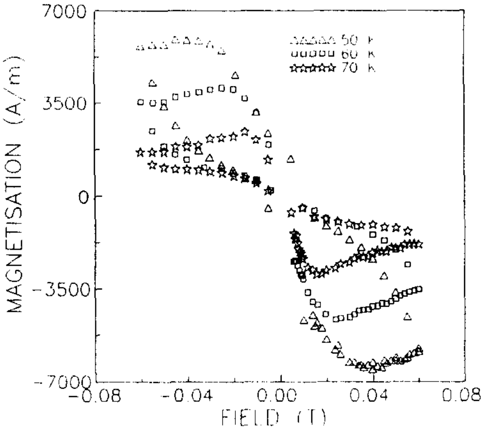

Fig.2

The field dependence of magnetization of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ at 50, 60 and 70 K, respectively

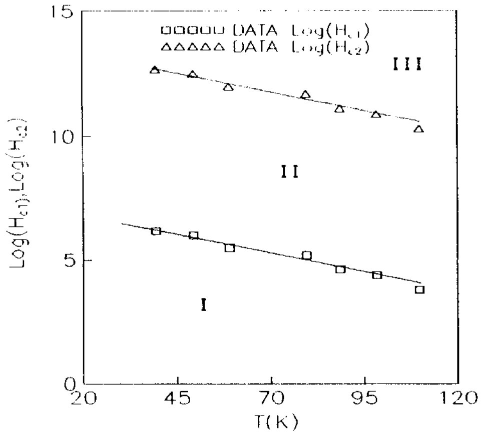

Fig.3
The H-T diagram , the temperature dependencies of upper and lower critical fields of sample $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$.

The fields higher than 5 mT bring into effect a full shielding of phase with critical temperature 65 K (Fig.1). The hysteresis curve in magnetization $M_{ZFC}(B)$ at temperatures 50, 60, and 70 K are shown on Fig.2. The measurement have been carried out at Faraday balance setup (Oxford Instruments Susceptibility System).

The hysteresis loops have a typical character as a metal-oxides bismuth systems. The hysteresis loop area decrease with increasing temperature, the loop area represent an energy of superconductor in the magnetic field. The value H_{c1} (T=const.) was determined from dependence $B^{1/2}=f(H)$ where sharp break corresponds to the lower critical field H_{c1} [9].The thermodynamic field H_{cT} we calculated from hysteresis loop area $S=H_{cT}^2/8*\pi$, standardized to sample volume.

The upper critical field we calculate from relation $H_{c1}*H_{cT}=H_{c2}^2$, effective London penetration depth λ_{eff} and the effective coherence length ξ_{eff} we determined from relation (1) and (2).

$$\lambda_{eff} \cong [\,\frac{\Phi_0}{H_{c1}}\,]^{1/2} \tag{1}$$

$$\xi_{eff} \approx \lambda_{eff} * \exp[-4*\pi*\lambda_{eff}^2*\frac{H_{c1}}{\Phi_0}] \tag{2}$$

Φ_0, $\kappa=\lambda_{eff}/\xi_{eff}$ are the flux quantum and the parameter (G-L) Ginzburg-Landau, respectively.

The H-T diagrams of HTSC $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ are displayed on figure 3. The existence of critical magnetic fields of HTSC with arbitrary mechanisms of superconductivity is a result of generally thermodynamical conditions. The HTSC are superconductors of second type, $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ belongs to this group too. The curves $H_{c1}(T)$ and $H_{c2}(T)$ divide a H-T thermodynamical area into three parts, the first part represents a Meissner state of superconductor (I), the second mixed state (II) and the third the normal state of superconductor (III). The determining of mechanisms of superconductivity is possible by detail analysis of temperature and field dependencies of critical fields H_{c1}, H_{c2} and parameters obtained from G-L theory. The temperature dependencies of H_{c1} and H_{c2} for our samples follow relation $H_{ct}=H_{ct0}*\exp[-T/T_{i0}]$ where for i=1, H_{c10}=1616 Oe, T_{10}=33.15 K and for i=2 $H_{c20}=1.0937*10^6$ Oe, T_{20}=33.15 K. The temperature dependence of critical thermodynamical field is analogous with parameters H_{cT0}=5310 Oe, T_{T0}=33.15 K. The value $J_c(0)$ was obtained by interpolation (in the Bean's terms) from dependence $J_c=J_c(0)*\exp[-T/T_0]$, where $J_c=30*(M^+-M^-)/d_0$, d_0 is average the size of grain, M^+, M^- are the magnetization of superconducting sample in the field increasing and

Tab. I

Bismuth HTSC	T_c [K]	$H_{c1}(0)$ [Oe]	$H_{cT}(0)$ [Oe]	$H_{c2}(0)$ [kOe]	$\lambda_L(0)$ [μm]	ξ (0) [Å]	$J_c(0)$ [A/cm^2]	κ [a.u.]
2234	108	1616	5310	109.4	0.085	16.59	$5.6*10^7$	≅ 49
2223	110	298	-	100.0	0.220	18.60	$1.3*10^6$	≅118
2212	≅ 85	≅ 120	-	20-70	0.3-3.7	≅20.40	$1.2*10^6$	≅147

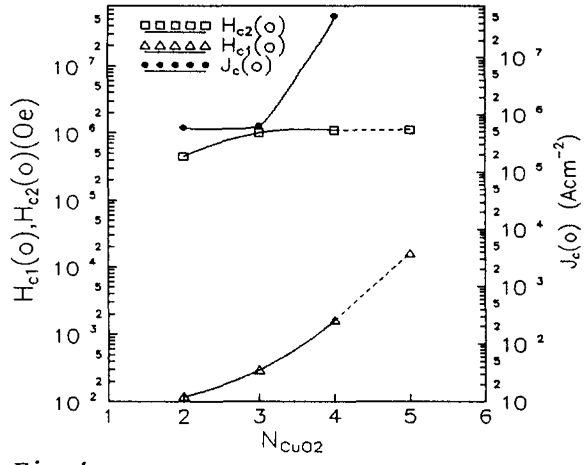

Fig.4

The dependencies of critical fields H_{c1}, H_{c2} and critical current density J_c as function of number of CuO_2-layers for the $Bi_{1.6}Pb_{0.4}Ca_3Cu_4O_{12+y}$ sample.

decreasing, respectively.

The figure 3 shows no saturation of critical fields $H_{c1}(T)$, $H_{c2}(T)$ for lower temperatures, it means the deviation from BCS model. In spite of the all results can be explained in terms BCS theory, if we assume the layers structure of HTSC with the small coherence length (small compare to the layers distance in c-axis direction). The CuO_2 layers are superconducting and SrO, CaO and CuO are in normal state. The small distance of superconducting and normal layers brings on that normal layers become a superconductive (proximity effect). The temperature dependence of critical field H_{c1} is characteristic without saturation for lower temperatures in case the proximity effect [10]. On the Fig.4 are displayed the dependencies of critical fields H_{c1}, H_{c2} and the critical current density J_c for bismuth HTSC as function of the number CuO_2 layers in elementary cell.The all values of critical parameters increase with increasing of number of CuO_2-layers in superconductors. The samples $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ are characterized by the higher values of critical parameters (critical fields H_{c1}, H_{c2}, critical current density J_c) from among the superconductors of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ type.On the Fig.5 are displayed the dependencies of the coherence length, the London's penetration depth and the parameter Ginzburg-Landau for bismuth HTSC as function of the number CuO_2 layers in elementary cell.The results of our measurements on the samples $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12+y}$ (2234) are shown in table 1. For comparing we list the parameters for 2212 and 2223 bismuth system too [11].

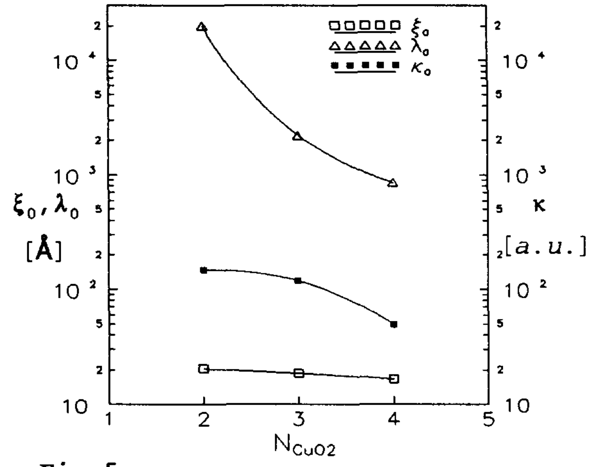

Fig.5

The dependencies of coherence length, London's penetration depth and parameter Ginzburg-Landau as function of number of CuO_2-layers for the $Bi_{1.6}Pb_{0.4}Ca_3Cu_4O_{12+y}$ sample.

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