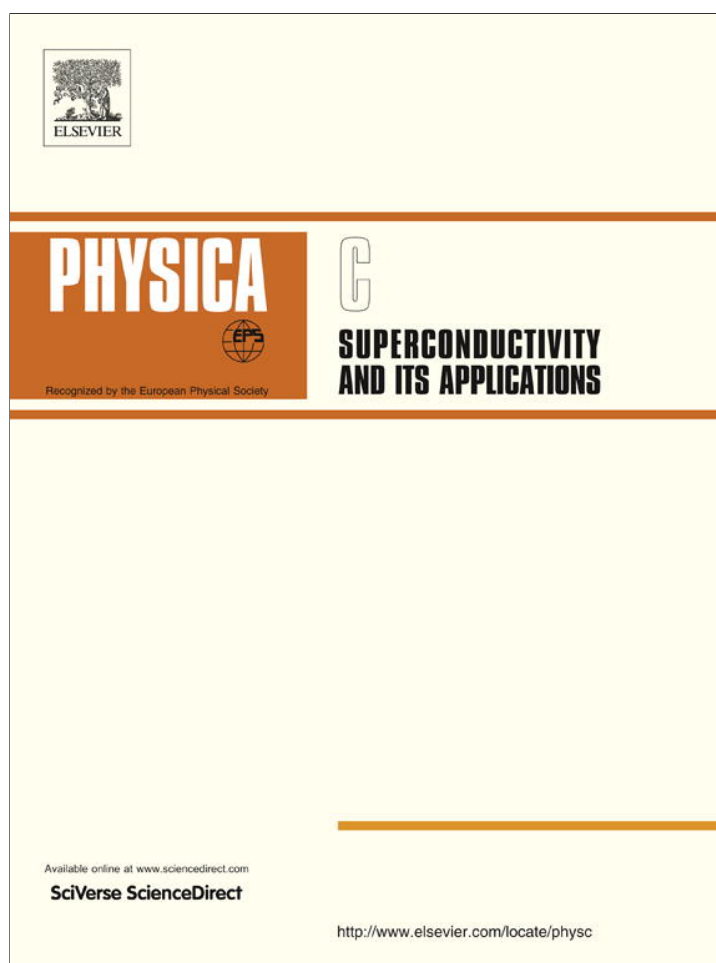


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The superconducting properties of nanostructured Pb₇Bi₃ films obtained by pulse electroplating

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ABSTRACT

Nanocrystalline films of submicron thickness of the Pb–Bi alloy, including those of intermetallic compound Pb₇Bi₃, are obtained by means of pulsed current electroplating on the basis of complex-forming organic solvent, as well as of aqueous electrolyte basing on trilonate complex of lead and bismuth. The component (EDX) and phase (XRD) structure of films, the morphology of their surface are characterized. The dependence of electrical resistance of films from temperature and the temperatures of superconductivity state (T_c) are measured. The films with the average grain size of 300 nm and $T_c = 7.8$ K are obtained with organic electrolyte containing lead and bismuth salts. Additional input of Ce³⁺ salt into the organic electrolyte allows obtaining films with T_c increased upto 10.3 K. The films with the T_c risen up to 9.0 are also obtained by pulsed current electroplating from aqueous electrolyte. The increase of T_c in Pb₇Bi₃ films is associated with their nanocrystalline structure.

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1. Introduction

At present times, vacuum sputtered layers of metallic superconductors (Nb, Al, Pb, MoGe, etc.) are used as the superconducting elements of new electronic schemes [1]. In some of the tasks related to the use of normal metals a method of electroplating from solution is implemented. A good example of that is creating multi-layer metallic structures [2] and growing nanosized threads in porous matrix [3]. Many technological problems connected with the technique of superconducting materials vacuum sputtering could have been avoided if the method of electroplating from solution was used instead. However, electroplating of Nb layers from solutions under regular conditions is still an unaccomplished task, and frequently used lead layers with nanometer thickness oxidize easily, losing their superconducting properties. At the same time, intermetallic compound Pb₇Bi₃ is more resistant to oxidation and has a superconducting transition temperature $T_c = 7.8$ K, however, the written sources do not provide any examples of obtaining nanocrystalline films of this junction by the method of pulsed current electroplating.

Our approach to obtaining metallic alloy layers consists of using electrolytes on the basis of complex-forming aprotion-dipolar solvent, which allows us to obtain films from alloys (including intermetallic compounds ones) both in electroless process [4] and using the method of pulse electroplating [5]. The distinctive feature of thin films obtained under such conditions is their nanocrystalline

structure. We were also developing the methods of electroplating of Pb₇Bi₃ nanocrystalline films and nanowires by pulse electroplating from aqueous electrolyte.

The main goal of the present study is the development of the PbBi electroplating techniques of nanocrystalline films and investigation of their superconducting properties.

2. Experimental

2.1. Electroplating method

Pb₇Bi₃ films with the characteristic thickness of 20–100 nm were grown from the solution on brass and copper substrates using pulse electroplating. The sample of 5 cm² was used as a cathode whereas platinum foil had the role of the anode. Rectangular current pulses were sent through the electrolyte solution, the amplitude of 50–900 mA and pulse length 3–50 ms were controlled via computer interface. The current density was varied in the range of 10–180 mA/cm². The electrolyte contained ions of Pb²⁺, Bi³⁺ or Pb²⁺, Bi³⁺ and Ce³⁺ in organic aprotion-dipolar solvent [4,5]. The organic aprotion-dipolar solvent in combination with ammonium chloride (0.3–0.6 m/l) provides the complex-forming process with ions of lead, bismuth and cerium in the electrolyte, which allows obtaining thin films of PbBi alloys as the result of electroplating. The amount of Pb and Bi in the grown films was adjusted by changing the current density as well as the concentration of metal ion in the solution. The intermetallic Pb₇Bi₃ was grown from the electrolyte containing 0.03 mol/l of Pb²⁺ and 0.02 mol/l of Bi³⁺. The current density and electrolyte temperature during the electroplating were

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10–180 mA/cm² and 60 °C respectively. During the deposition the electrolyte was also carefully agitated. The table represents the electrolyte composition and electroplating conditions for each sample.

2.2. Characterization techniques

The transport and superconducting properties of the obtained films were measured using standard 4-point scheme. The resistance of the films was examined at different temperatures from 300 K down to the superconducting transition around 7.8 K and then the critical field H_{c2} was measured at 4.2 K. SEM Supra V50 and Siemens D500 systems were used for the investigation of the film composition, morphology and X-ray analysis (Cu $K\alpha$ -radiation) respectively.

3. Results and discussion

The experimental conditions of growing, component structure of the electrodeposited films and measured T_c are represented in Table 1.

The found electrolyte formula and the electroplating regime ensure obtaining films of intermetallic Pb_7Bi_3 . Fig. 1 shows the diffraction pattern of Pb/Bi -71/29 at.% film, grown on brass substrate by pulse electroplating, the film thickness is 80 nm. The X-ray analysis reveals the single phase surface Pb_7Bi_3 , which has a hexagonal close-packed structure (S.G. P63 mmc) having the following lattice parameters $a = 3.5058 \text{ \AA}$, $c = 5.7959 \text{ \AA}$ respectively, and texture parallel to (101) plane.

The film surface morphology of sample is presented in Fig. 2. SEM image of sample No. 1 demonstrates the average grain size of 300 nm. The dependence of the film resistance versus temperature is quite predictable, see Fig. 3a, and demonstrates the superconducting transition around $T_c = 7.8 \text{ K}$, which agrees well with the data for bulk intermetallic Pb_7Bi_3 .

When adding 0.057–0.189 m/l of Ce^{3+} salt to the electrolyte films of intermetallic compound Pb_7Bi_3 with a slight addition of bismuth as a second phase (EDX and XRD analyses) are obtained reproducibly. T_c of various samples of such films display values ranging from 9 to 10.3 K (see Table 1 and Fig. 3b).

To characterize the sample No. 2 with the $T_c = 10.3 \text{ K}$ was also following measured. At 4.2 K, well below the superconducting transition, the critical field H_{c2} is reached around 7kOe if the external magnetic field is applied perpendicular to the film surface (Fig. 4).

It is also apparent from the EDX-analysis results that cerium is either not present in films or its quantity (samples Nos. 3 and 4)

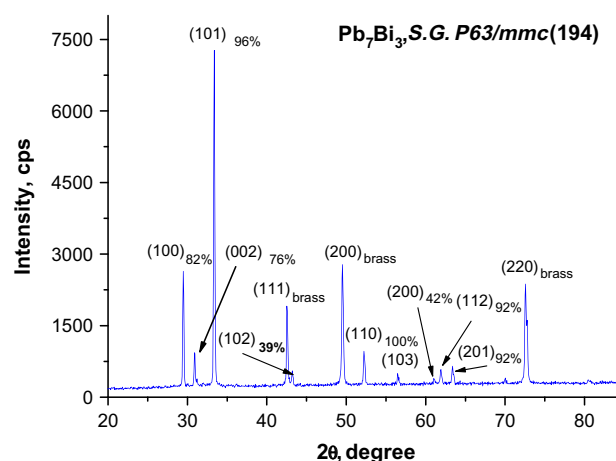


Fig. 1. The diffraction pattern of Pb/Bi -71/29 at.% film, grown on brass substrate by pulse electroplating. The percentages in the peaks indicate the intensity of the reflections [6]. 20, 30, 40, 50, 60, 70, 80, 0, 1500, 3000, 4500, 6000, 7500, (112) 92%, (200) 42%, (220) brass intensity, cps 2, degree (100) 82%, (002) 76%, (101) 96%, (102) 39%, (111) brass, (110) 100%, (103) (201) 92% Pb_7Bi_3 , S.G. P63/mmc (194).

lies within the detection limit of the method, i.e. there is no correlation.

At the same time, SEM-analysis of the sample morphology revealed that films grown with electrolyte containing cerium salt have the average crystallite grain size ranging from 10 to 30 nm, the sample No. 2 show the grain size around 20 nm.

The grain size reduction is explained by the fact that the electroplating of the film takes place at electroreduction of the cathode of form complex compound $[Ce(DMSO)_8]^{3+}[BiCl_6]^{3-}$ where Bi^{3+} is in anion. The electroplating from the complex happens, as it is known, at increased potential and is used for obtaining microcrystalline precipitate. In confirmation of this, by means of pulsed current electroplating in ultrasonic bath with a high current density, a Pb_7Bi_3 film with $T_c = 9.0 \text{ K}$ was obtained from aqueous electrolyte with complex compounds where ions Pb^{2+} and Bi^{3+} were bound in form complex compounds with complex-forming agents 2Na-EDTA and Na-gypophosphite. SEM image of film surface samples No. 8 (Fig. 2c) shows the nanocrystalline structure also, the crystallites are in this case the form of thin plates and needles, the average grain size of 50–70 nm.

4. Conclusions

The films of submicron thickness from intermetallic compound Pb_7Bi_3 with $T_c = 7.8 \text{ K}$ were obtained by means of pulsed current

Table 1

The main parameters of the pulsed current electroplating, composition and T_c of the film. J is the current density pulses, n is the number of pulses passed, ν is the pulsed current frequency, d.c. = $100 T_{on}/(T_{on} + T_{off})\%$, (where T_{on} – pulse duration, T_{off} – pause between pulses) is the pulse duty-cycle.

| No. | Concentration of ions in the electrolyte (mMol/l) ^a | | | Electroplating parameters | | | | Composition of the coating (at.%) | | | T_c (K) |
|-----|--|-----------|----------------|---------------------------|----------|------------|-------|-----------------------------------|------|-----|-----------|
| | Pb^{2+} | Bi^{3+} | Ce^{3+} | J (mA/cm ²) | d.c. (%) | ν (Gc) | n | Pb | Bi | Ce | |
| 1 | 0.030 | 0.020 | – | 67 | 50 | 166.6 | 5000 | 72.4 | 27.6 | – | 7.8 |
| 2 | 0.033 | 0.016 | 0.057 | 65 | 50 | 166.6 | 5000 | 71.1 | 28.9 | – | 10.3 |
| 3 | 0.033 | 0.016 | 0.091 | 83 | 50 | 166.6 | 5000 | 66 | 34 | – | 9.0 |
| 4 | 0.036 | 0.019 | 0.115 | 30 | 85.7 | 28.6 | 10000 | 69.9 | 30.1 | 0.3 | 9.0 |
| 5 | 0.036 | 0.019 | 0.189 | 32 | 85.7 | 28.6 | 6000 | 69.5 | 30.5 | 0.3 | 9.3 |
| 6 | 0.033 | 0.016 | 0.057 | 86 | 83.3 | 55.5 | 6000 | 68.2 | 31.8 | – | 10.0 |
| 7 | 0.036 | 0.019 | 0.236 | 10 | 97.1 | 9.7 | 3000 | 67.2 | 32.8 | – | 9.0 |
| 8 | 0.066 | 0.033 | – ^b | 180 ^c | 23.1 | 76.9 | 2300 | 63.4 | 36.6 | – | 9.0 |

^a 1–7 – DMSO solutions; and 8 – aqueous solution.

^b 0.130 mMol/l 2Na-EDTA + 0.076 mMol/l Na-gypophosphite as complexing agents.

^c In an ultrasonic bath.

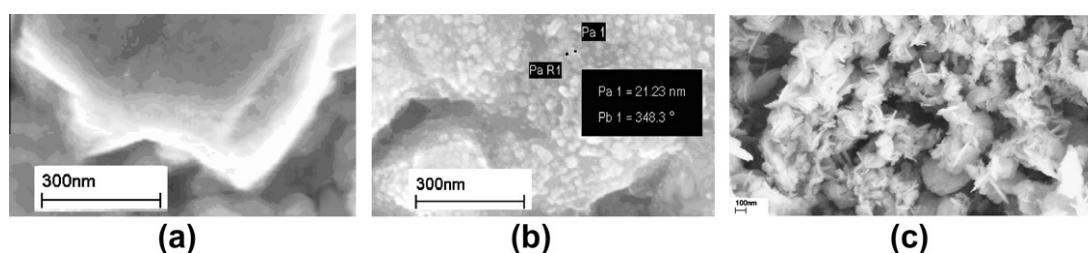


Fig. 2. SEM images of films surfaces of sample Pb_7Bi_3 : (a) the sample No. 1 obtained from organic electrolyte without Ce^{3+} ; (b) the sample No. 2 obtained from organic electrolyte with Ce^{3+} ; and (c) the sample No. 8 obtained from aqueous electrolyte.

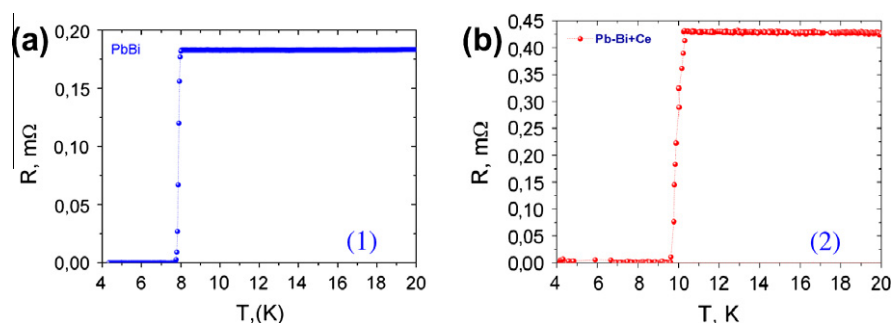


Fig. 3. Temperature dependence of resistance for Pb_7Bi_3 film: (a) the sample No. 1 obtained from organic electrolyte without Ce^{3+} ; and (b) the sample No. 2 obtained from organic electrolyte with Ce^{3+} .

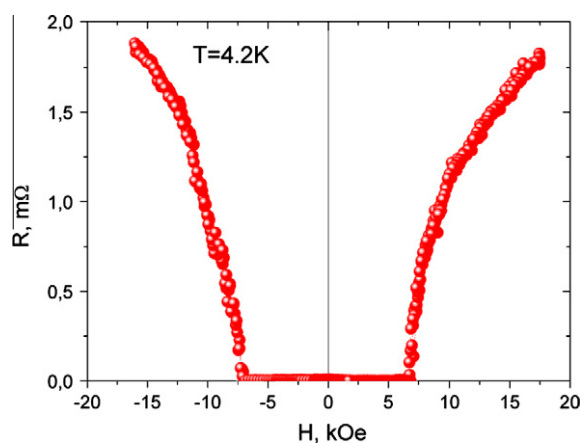


Fig. 4. Field dependence of resistance for Pb_7Bi_3 film (the sample No. 2 obtained from organic electrolyte with Ce^{3+}).

electroplating of lead and bismuth from a proton-dipolar complex-forming solvent on brass and copper substrates. The solutions containing cerium salt with same conditions allow obtaining films that contain 28.9–32.8 at.% of bismuth displaying $T_c = 9$ and 10 K. EDX-analysis does not reveal cerium in the films, or its quantity (0.3 at.%) is on the border of the detection limit of the method. XRD shows that the films consist of intermetallic Pb_7Bi_3 with the admixture of bismuth phase. Considering that bismuth $T_c = 6.17$ K, that the amount of bismuth phase is less than 5–6%, insufficient for percolation, and, lastly, considering that the observed transitions are relatively narrow and comprise less than

1 K, we cannot attribute the increase of T_c to the presence of the admixture in question. At the same time SEM-research revealed that films obtained from electrolytes containing cerium salt, are characterized by the nanocluster 20–30 nm grain structure. Therefore, the increase of T_c is correlated, obviously, with the nanocrystalline structure of the films. Such possibility was supposed in the theoretical work [7]. The influence of the cerium salt lies in its Ce^{3+} ion comprising a form ionic complex $[\text{Ce}(\text{DMSO})_8]^{3+}[\text{BiCl}_6]^{3-}$ in the solution, where Bi^{3+} is in anion. It is known that electroreduction of such complex anions on the cathode happens with a potential shift of electroplating into the negative region and leads to fine-grain precipitate. As a confirmation of this we managed to obtain a Pb_7Bi_3 film with $T_c = 9$ K by means of pulsed current electroplating from aqueous solution where ions Pb^{2+} and Bi^{3+} are bound in form complex compounds with complex-forming agents 2Na-EDTA and Na-glycophosphite. The Pb_7Bi_3 film have the nanocrystalline structure also in this case.

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