Possible High T_c Superconductivity in Ag Doped PbO_1+y (0.4

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Preliminary Communication

Possible High T_c Superconductivity in Ag Doped $PbO_{1+\delta}$ ($0.4 < \delta < 0.6$)

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We have found that the doping of Pb_3O_4 with silver and its treatment in elevated oxygen pressure result in a number of novel metallic phases. The $Pb_{1-x}Ag_xO_{1+\delta}$ phases ($0.4 < \delta < 0.6$; $x \approx 0.1$–0.15) prepared at 260–330 °C exhibit electric and magnetic properties compatible with the indication of superconductivity (SC), which appears at $T_c \approx 285$ K. SC can be attributed to Ag doped lead sesquioxide $Pb_{2-x}Ag_xO_{3-y}$ ($y \approx \pm 0.2$).

Recently, we published[1,2] the resistive properties of the CuO–PbO–Ag_2O system with resistive transitions which point to the possible novel high T_c superconductors with T_c higher than 200 K. In the meantime, it was clear that CuO and PbO do not mix even at temperatures above 800 °C.[3] Since resistivity downturns below 285 K are also present in samples in which CuO is absent, we concentrated our study on the Pb–Ag–O system prepared at different O_2 pressures.

Investigations of binary oxides $Ag_5Pb_2O_6$ and Ag_2PbO_2 (Ref. 4) have revealed good metals but no SC has been evidenced.

In this letter, we describe one of the several preparation routes, most successful in obtaining novel superconductors[#] so far.

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[#] Throughout this letter SC events refer only to samples for which resistance downturns are accompanied by an appearance of diamagnetism below RT.

The starting components were powders of Pb_3O_4 prepared from tetragonal (red) PbO (Johnson Matthey, *p.a.*) at 430 °C in air and Ag_2O (*purissimus* grade) mixed in appropriate proportions in order to obtain different doping concentrations x = Ag/Pb. The powders were pressed in pellets using 4 kbar uniaxial pressure and heated up to 260–330 °C for ≈1 hour at different oxygen pressures (2–50 bars). The samples were then cooled to RT at a rate of ≈50 °C/hour and four probe electric resistance measurements were performed in the standard way using 15 microns gold wires and silver paint. The room temperature (RT) resistance data are shown in Figure 1. A dramatic decrease of resistance is evident at $x_m \approx 0.10$. In a rather narrow range of concentration, $\Delta x \approx 0.01$, the resistance decreased by more than seven orders of magnitude. A slight increase of R with concentration x was recorded for $x > x_m$. For $x < x_m$ samples behave as semiconductors if cooled below RT while for $x > x_m$ the metallic properties are obeyed.

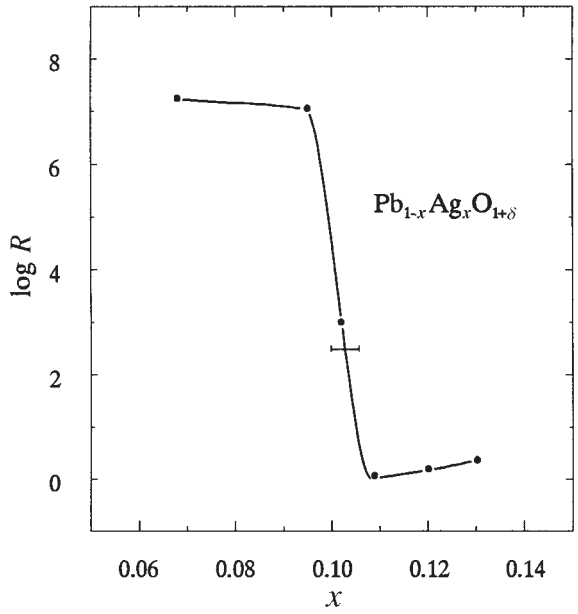

Figure 1. Electric resistance of $Pb_3O_4 + Ag_2O$ at RT dependent on x = Ag/Pb.

The X-ray diffractograms recorded on Phillips PW 1710 diffractometer with CuK_α radiation showed the presence of Pb_3O_4 as major phase, Pb_2O_3 and undissolved Ag_2O. The strongest diffraction lines ascribed to Pb_2O_3 are $hkl = 200$, d = 3.208 Å, hkl = 012, d = 2.957 Å and hkl = 020, d = 2.812 Å and the estimated unit cell is a = 7.812 Å, b = 5.631 Å and c = 8.464 Å with β = 124,75° in agreement with earlier results.[5]

When cooled to liquid nitrogen (LN_2) temperatures, some samples (nearly 10% of preparation runs) exhibited resistivity transitions, as it is shown ($x = 0.12$) in Figure 2a. For measuring current ≈1 mA and $T < 270$ K, the resistivity was less than 1 μΩ cm. At ≈190 K, the magnetic field of ≈105 gauss was switched on and the sample reheated. Apparent dependence on the magnetic field is visible in the heating cycle (Figure 2b). By repeated cooling in zero field, the resistance curve (Figure 2a) is reestablished. The aberation from the general behaviour of five points at $T \geq 200$ K is unclear. For PbO (Ref. 6) and Pb_3O_4 (Ref. 7), the authors report a ferroelectric transition at $T \approx 200$ K. Such a transition may not be excluded in Pb_2O_3 either and the cited discrepancy may have a systematic origin.

Some samples, when cooled in liquid nitrogen, deflected in the presence of the Co_5Sm permanent magnet. Finally, the preliminary test of alternating current (AC) susceptibility performed on a compensating secondary coil susceptometer at 77 K resulted in the evidence of diamagnetic fraction which corresponds to nearly 11 percent of the total sample volume. All samples are sensitive to temperature cycling between RT and liquid nitrogen

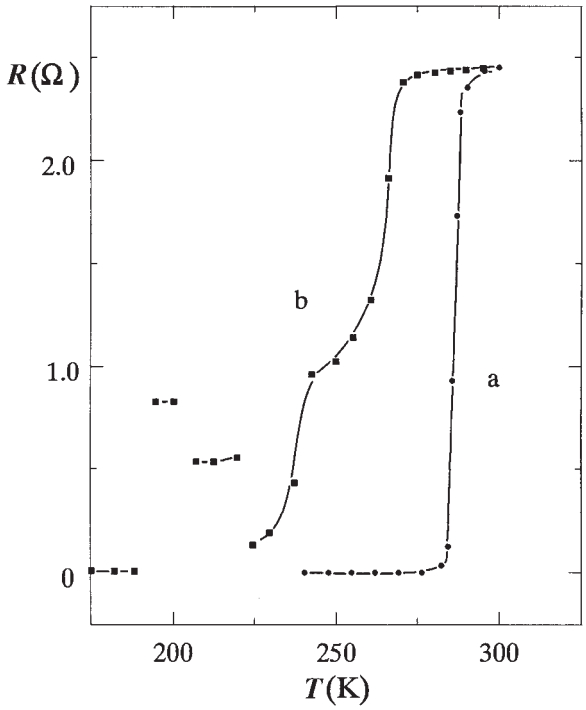

Figure 2. Temperature dependence of electric resistance at $T < 300$ K (1 mA measuring current): a) by cooling; b) by heating at $B = 105$ gauss.

bath and after several cycles SC effects gradually disappear, probably as a result of inhomogeneity, which is accompanied by redistribution of dopand within the grains.[#] This possibility is supported by some experiments in which SC events are induced by the application of ≈2 kbar uniaxial stress to powders. Deterioration of SC is weaker if the cooling is not performed below 200 K.

Decomposition of SC samples on the thermogravimetric (TG) balance by heating in air is shown by curve (a) in Figure 3. The first slightly decreasing step corresponds to the decomposition of undissolved Ag_2O. The second step beginning at ≈425 °C is due to the oxygen loss from $Pb_{2-x}Ag_xO_{3-y}$ during the extraction of Ag. Our estimate is $y \approx \pm 0.2$. Finally, the last step at 570 °C points to the beginning of decomposition of Pb_3O_4 to PbO.

The decomposition curve of Pb_3O_4 with $x < 0.1$ and when the sample is insulator is shown by curve (b) in Figure 3. The first step corresponds to an extraction of Ag and the corresponding loss of oxygen. The X-ray diffractograms obtained on samples taken from the TG balance at temperatures between 470 °C and 570 °C clearly confirmed Pb_3O_4 and elementary silver.

The electric resistance of the samples heated up to 400–440 °C diverges at infinity (inset of Figure 3). This strongly supports the assumption that

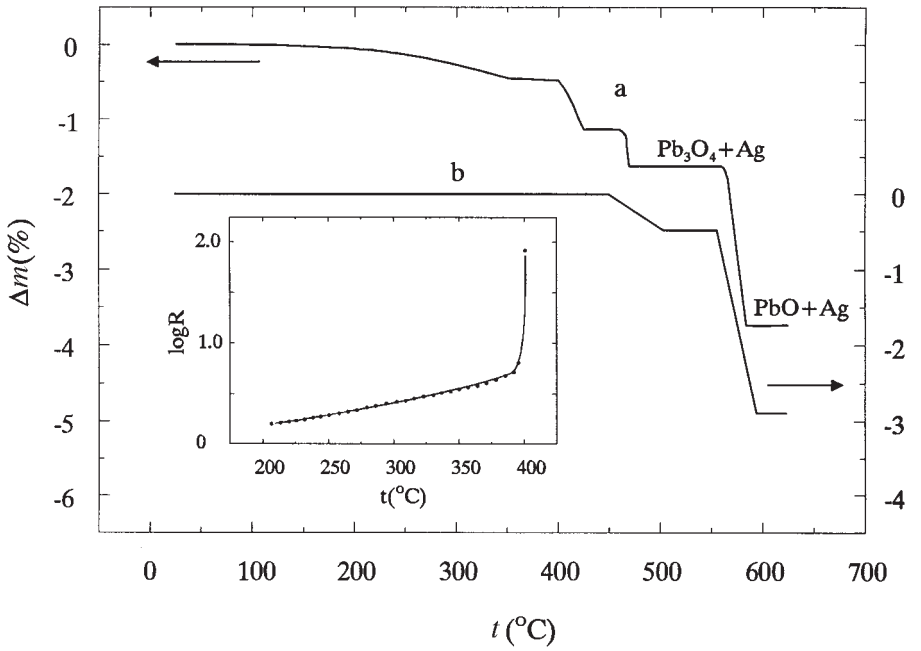

Figure 3. Thermogravimetric decomposition of: a) Ag doped Pb_3O_4+Ag doped Pb_2O_3 (nominal $x = 0.12$); b) Ag doped Pb_3O_4 (nominal $x = 0.09$). The inset shows the temperature dependence of resistance (up to degradation at 400–440 °C) in sample a.

Pb_2O_3 possibly carries the SC phase. In addition to this assumption, the samples without the first decomposition step at 425 °C are not superconducting. No SC properties were observed in samples containing only Ag doped Pb_3O_4 phase, either.

The instability of samples may be attributed to the difficult preparation of Pb_2O_3 by simple oxidation of Pb_3O_4 even by oxygen pressures as high as several hundreds of bars for several weeks. In our experiments, Pb_3O_4 can be partly oxidized to Pb_2O_3 in the presence of Ag_2O at elevated oxygen pressures.

In conclusion, Pb_3O_4 doped with Ag transforms from the insulating to metallic state at $x \approx 0.1$. At elevated oxygen pressures (2–50 bars), this kind of metal partly takes up additional oxygen to $Pb_{1-x}Ag_xO_{1.4}$ with the structure which points to lead sesquioxide Pb_2O_3. The samples showing characteristic X-ray diffractions lines of Pb_2O_3 point to the indication of SC appearing at ≈285 K.

Preparation of pure Pb_2O_3 and its subsequent doping with Ag is in progress.

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Note added in proof:

In the meantime we have prepared Pb_2O_3 by hydrothermal decomposition of PbO_2 (310 °C, 450 bar of water) with the final yield of about 70–80 molar percents Pb_2O_3 and remaining PbO_2. An addition of Ag_2O to the Pb_2O_3-PbO_2 mixture and heat treatment at 350 °C (200 bar O_2) results in the appearence of SC. Subsequent heating up to 620 °C in oxygen pressure 200–500 bar, substantially improves the stability of samples. An assumption that Ag doped Pb_2O_3 carries possible superconductivity seems to be correct.

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SAŽETAK

Moguća supravodljivost s visokom T_c u Ag-dopiranom $PbO_{1+\delta}$ ($0.4 < \delta < 0.6$)

Danijel Djurek, Zvonko Medunić, Anton Tonejc i Matija Paljević

Našli smo da Pb_3O_4, dopiran srebrom, pod povišenim tlakom kisika daje nove metalne faze. Faze $Pb_{1-x}Ag_xO_{1+\delta}$ ($0{,}4 < \delta < 0{,}6$; $x \approx 0{,}1$–$0{,}15$) pripremljene na 260––330 °C pokazuju električna i magnetska svojstva suglasna mogućoj supravodljivosti s $T_c \approx 285$ K. Supravodljivost se može pripisati srebrom dopiranom oksidu $Pb_{2-x}Ag_xO_{3-y}$ ($y \approx \pm 0{,}2$).