Tin-based high-temperature superconductor

K. S. Aleksandrov, A. D. Vasil'ev, S. A. Zvegintsev, S. N. Krivomazov, M. I. Petrov, and B. P. Khrustalev

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR

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A tin-based superconducting ceramic with $T_c \sim 86$ K has been synthesized. A study of the electrical and magnetic properties of the resulting samples is reported.

In this letter we discuss high-temperature superconductors whose layered structure is formed by elements with an "unshared electron pair." The first high-temperature superconductors to be synthesized from compounds of this type were based on bismuth[1–3]; a superconductivity in thallium-based compounds was subsequently observed.[4] One might suggest that other ions with an unshared-pair effect would be capable of forming superconducting oxide compounds of copper. Reports of the observation of a superconductivity in compounds containing lead have recently appeared.[5,6]

We are reporting here the results of a search for superconductivity in compounds based on tin, which also has an unshared electron pair. This search has resulted in the discovery of superconductivity in certain compounds of the Sn–Ba–Sr–Y–Cu–O system. The alkaline-earth elements are used in this system because they play a major role in forming the superconductivity, as stabilizers of the highly oxidized state of the copper cations.[7]

The following compounds were synthesized: $Sn_1Ba_1Sr_1Cu_3O_x$, $Sn_1Ba_1Ca_1Cu_3O_x$, $Sn_1Ba_1Mg_1Cu_3O_x$, $Sn_1Sr_1Ca_1Cu_3O_x$, $Sn_1Sr_1Mg_1Cu_3O_x$, and $Sn_1Ca_1Mg_1Cu_3O_x$. The original substances were SnO_2, BaO_2, $SrCO_3$, $CaCO_3$, MgO, and CuO. We used a multistep ceramic procedure. The final firing was at 960 °C for 12 h. The samples were then cooled with the oven. All sythesis cycles were carried out in air.

Of the compounds synthesized, only $Sn_1Ba_1Sr_1Cu_3O_x$ exhibited a significant conductivity ($\rho \approx 10\ \Omega\cdot$cm) at room temperature. (The other compounds were essentially insulators, with $\rho > 1000\ \Omega\cdot$cm.) At $T < 100$ K we observed a diamagnetic response of the sample, with a Meissner phase having a relative volume $\sim 2\%$.

Taking up the problem of increasing the concentration of the superconducting phase, we carried out a partial substitution of monovalent potassium and trivalent yttrium for the divalent barium and strontium cations. The cation ratio was not changed. we synthesized and studied two sample: $Sn_1Ba^{0.7}Sr_{0.7}K_{0.7}Cu_3O_x$ and $Sn_1Ba_{0.7}Sr_{0.7}Y_{0.7}Cu_3O_x$.

The first of these samples turned out to be a typical paramagnet, without any anomalies down to 4.2 K.

The second sample exhibited magnetic and electrical properties which are unambiguous evidence that the sample contains a superconducting phase. Note that the

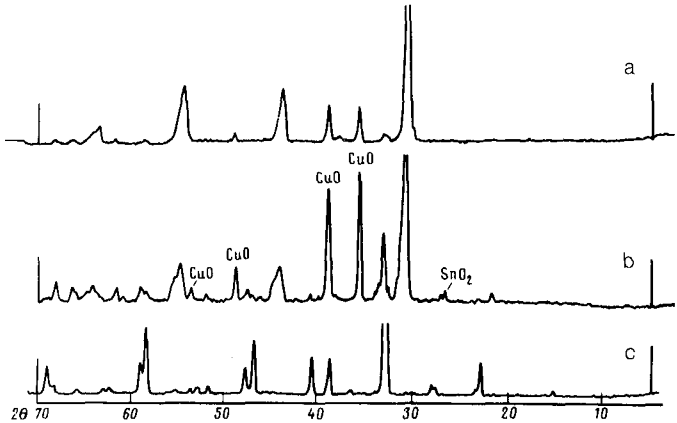

FIG. 1. Debye patterns of samples of the following compositions: *a*—$Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$; *b*—$Sn_1Ba_{0.7}Sr_{07}Y_{0.7}Cu_3O_x$; *c*—$Y_1Ba_2Cu_3O_{7-\delta}$.

superconductivity was observed in a sample containing yttrium. We thus cannot rule out the possibility that the $YBaSrCu_3O_7$ phase formed in the sample; according to Ref. 8, it could cause the observed superconductivity. An x-ray phase analysis did not unambiguously rule out the presence of this phase (see the Debye patterns in Fig. 1). We believe, however, that the superconducting properties of this sample are not a consequence of that phase. This conclusion follows from a study of the properties of $Sn_2Sr_2Ba_{0.5}Y_{0.5}Cu_3O_x$, and $Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$, samples synthesized by analog with the compound $Pb_2Sr_2(Y,Ca)_1Cu_3O_8$, in which superconductivity has been reported.[5,6] It may be that the probability for the formation of the $YBaSrCu_3O_7$ phase which we mentioned above is the same in the two samples, but their electrical properties turn out to be quite different. The compound $Sn_2Sr_2Ba_{0.5}Y_{0.0}Cu_3O_x$ is an insulator, and we will not discuss its properties here. The second of these compounds has well-expressed superconducting properties. Its Debye pattern is shown in Fig. 1a; shown in the same figure are Debye patterns of the $Sn_1Ba_{0.7}Sn_{0.7}Y_{0.7}Cu_3O_x$ samples (Fig. 1b) and, for composition, of $Y_1Ba_2Cu_3O_7$ (Fig. 1c).

A comparative analysis of these spectra suggests that the Sn–Ba–Sr–Y–Cu–O compound retains the basic structural motif of $Y_1Ba_2Cu_3O_7$. The tentative values of the unit-cell parameters of the $Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$ crystal are $a \approx 4.1$ Å and $c \approx 12.4$ Å (or a multiple of this value). The reflection with $2\theta = 33°$ in the spectrum in Fig. 1b, which coincides with the strongest reflection in the $YBaSrCu_3O_{0.7}$ spectrum,[8] decreases in intensity by nearly an order of magnitude in the spectrum in Fig. 1a. This decrease is evidence that $YBaSrCu_3O_7$ does not contribute to the properties of the tin-bearing ceramics which we studied here.

Figure 2 illustrates the superconducting properties of $Sn_2Ba_2Sr_{0.5}Y_{0.5}Cu_3O_x$ with the temperature dependence of the magnetic moment, $M(T)$, recorded in a field $H = 100$ Oe. The shape of the curve indicates that the sample has superconducting properties at $T < T_c \approx 86$ K.

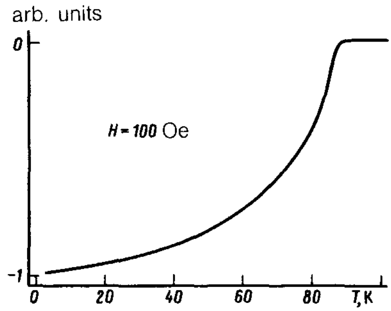

FIG. 2. Temperature dependence of the magnetic moment of a sample of composition $Sn_2Ba_2S_{0.5}Y_{0.5}Cu_3O_x$.

The superconducting phase amounts to ~15% of the volume of this sample, according to an estimate based on magnetic measurements with a powder.

The existence of a superconductivity in a tin-based system raises the hope that cations other than the familiar bismuth, thallium, and lead cations which have an unshared electron pair can form superconducting compounds. Within the category of oxides containing copper, each of these ions (mercury, antimony, indium, etc.) will correspond in the best way (for superconductivity) to one of the alkaline-earth ions (or to a combination thereof).

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