

High- T_c superconductivity in three-fluorite-layer copper oxides. I. (Hg,W)Sr₂(Ce,Eu)₃Cu₂O_{11+δ}

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(Received 19 February 2004; revised manuscript received 22 April 2004; published 17 November 2004)

A (Hg,W)-1232-phase copper oxide has been synthesized in an essentially single-phase form with the composition of (Hg_{0.7}W_{0.3})Sr₂(Ce_{0.58}Eu_{0.42})₃Cu₂O_{11+δ} through high-pressure synthesis at 5 GPa and 1100°C. The (Hg,W)-1232 phase contains a three-layer fluorite-structured block between adjacent CuO₂ planes. The crystal structure was confirmed by x-ray diffraction, high-resolution transmission-electron microscopy, and electron diffraction. In contrast to the previously known three-fluorite-layer copper-oxide phases, perfect diamagnetism with a large Meissner volume fraction was revealed for this (Hg,W)-1232 phase. The superconductivity transition temperature T_c was found at 33 K.

DOI: 10.1103/PhysRevB.70.174514

PACS number(s): 74.10.+v, 74.62.Bf

I. INTRODUCTION

The first high- T_c superconductor, (La,Ba/Sr)₂CuO₄, has a simple structure, where two rocksalt (RS) type AO layers with the A site randomly occupied by La and Ba/Sr alternate with a single CuO₂ plane. The two AO layers are rather flexible to sandwich additional oxygen-nonstoichiometric perovskite (P) or RS type MO_{1±δm} layers ($M = \text{e.g., Cu, Bi, Pb, Tl, Hg}$) to form a thicker “blocking block” of AO-(MO_{1±δm})_m-AO between two CuO₂ planes. The “superconductive block” may also get thickened having multiple CuO₂ planes piled up alternatively with layers of Q cation [$Q = \text{e.g., Ca, rare-earth element (R)}$]. This is the way the most common superconductive copper oxides with a layer sequence of AO-(MO_{1±δm})_m-AO-CuO₂-(Q-CuO₂)_{n-1} are formed. Such phases classified into “category A” obey a general chemical formula of $M_m A_2 Q_{n-1} \text{Cu}_n \text{O}_{m+2+2n\pm\delta}$ that may be abbreviated by $M-m^{(A)}2^{(Q)}(n-1)n$ or $M-m2(n-1)n$.^{1,2} At $n=2$, the two CuO₂ planes of the superconductive block may further accommodate an additional metal-oxide layer block, $B-(\text{O}_2-B)_{s-1}$ ($B=\text{Ce, other R, Sr}$), of a fluorite (F) type structure.³⁻⁵ The thus formed phases obey a layer sequence of AO[RS]-(MO_{1±δm})_m[P/RS]-AO[RS]-CuO₂[P]-[B-(O₂-B)_{s-1}][F]-CuO₂[P] (the additional letters in brackets refer to the structure of the layer) and comprise the second group of multilayered copper oxides, i.e., “category B.” From the layer sequence the general formula of a category B phase is derived at $M_m A_{2k} B_s \text{Cu}_{1+k} \text{O}_{m+4k+2s\pm\delta}$, where $m \geq 0$, $s \geq 1$ and $k=0$ or 1 (with the conditions that for $k=0$, $m=0$, and for $k=1$, $m \geq 0$). Furthermore, a phase obeying such formula may be denoted by $M-m^{(A)}(2k)^{(B)}s(1+k)$ or $M-m(2k)s(1+k)$.² As compared to category A phases, those of category B have been much less investigated. However, a versatile understanding of high- T_c superconductivity and the behavior of materials showing this phenomenon is not possible without extending the understanding over both categories of layered copper-oxide phases.

In Fig. 1 a schematic crystal structure of a category B phase is shown. In the known phases of category B, m varies from 0 up to 3, whereas s can be increased even up to 7 or 8

(though single-phase bulk samples have been realized only up to $s=3$).⁶⁻⁸ Phases with $s \geq 3$ are rather rare and none of them has been “superconductorized” yet.⁹ At the same time, no definite explanation has been given why these phases do not show superconductivity.¹⁰ In the present contribution clear evidence is provided that high- T_c superconductivity can be induced in a copper-oxide phase containing a three-layer fluorite block.

We focused our hunt for the “three-fluorite-layer superconductor” on Hg-containing systems. Among the category A phases, those with mercury at the “charge-reservoir” M -cation site have shown the highest T_c values.^{11,12} Also in the case of category B, the highest T_c of 75 K belongs to the Hg-based $s=2$ phase, i.e., (Hg_{0.75}W_{0.25})Sr₂(Ce_{0.25}Gd_{0.75})₂Cu₂O_z or (Hg,W)-1222.¹³ Even though the first samples of the (Hg, M')-1222 phase with various M' cations were reported already in

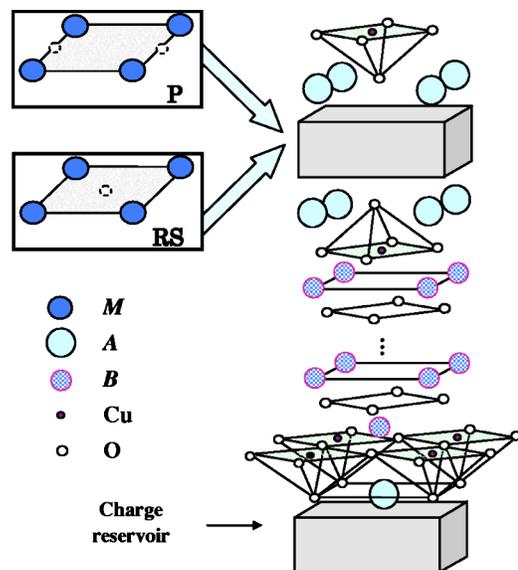


FIG. 1. Schematic illustration of the crystal structure of an $M_m A_{2k} B_s \text{Cu}_{1+k} \text{O}_{m+4k+2s\pm\delta}$ or $M-m(2k)s(1+k)$ phase of category B. Only the $M_m \text{O}_{m\pm\delta}$ charge-reservoir block of perovskite (P) or rock-salt (RS) type is believed to be oxygen nonstoichiometric.

1995,^{15,16} the Hg-based $s=3$ phase has remained to be uncovered up to now. Here we report both the successful high-pressure synthesis and the bulk superconductivity with $T_c \approx 33$ K of essentially single-phase samples of $(\text{Hg}, \text{W})\text{Sr}_2(\text{Ce}, \text{Eu})_3\text{Cu}_2\text{O}_{11+\delta}$ of the (Hg, W)-1232 phase.

II. EXPERIMENTAL

Samples of $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{1-x}\text{Eu}_x)_3\text{Cu}_2\text{O}_{11+\delta}$ with three different Eu contents of $x=0.33, 0.42$, and 0.50 were prepared by a two-step synthesis route. First, a precursor oxide of the cation composition of $\text{Sr}:(\text{Ce}, \text{Eu}):\text{Cu}=2:3:2$ was prepared from an appropriate mixture of SrCO_3 , CeO_2 , Eu_2O_3 (dehydrated prior to use at 1000°C for 10 h) and CuO by calcining at 900°C for 24 h in flowing O_2 gas, followed by slow cooling to room temperature. In the second step, nominal amounts of HgO and WO_3 were mixed with the Sr-(Ce, Eu)-Cu-O precursor. The thus obtained mixture was tightly packed into a gold capsule covered by a NaCl separator and placed into a pyrophyllite container equipped with an internal graphite heater. The high-pressure heat treatment was carried out at 5 GPa in a cubic-anvil-type apparatus at 1100°C for 30 min. After the high-pressure heat treatment, temperature was first quenched in ~ 10 sec and then pressure was slowly (within ~ 1 h) released.

The phase content and lattice parameters of the three samples were examined by x-ray powder diffraction (Rigaku: RINT2550VK/U; $\text{Cu } K_\alpha$ radiation). For the confirmation of the (Hg, W)-1232 crystal structure high-resolution transmission-electron microscopy (HRTEM) and electron diffraction (ED) were carried out using an ultrahigh-voltage transmission electron microscope (Hitachi H-1500) operated at an accelerating voltage of 820 kV. A specimen was prepared of the $x=0.42$ sample by crushing a portion of it into fine fragments, which were then ultrasonically dispersed in CCl_4 and transferred to carbon microgrids. Energy-dispersive x-ray (EDX) analysis was carried out under a field-emission transmission electron microscope (Hitachi HF-3000S) to determine the Hg:W and Ce:Eu ratios. Magnetic properties of the samples were measured at 10 Oe down to 5 K by a superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design: MPMS-XL) both in field-cooled (FC) and zero-field-cooled (ZFC) modes. Resistivity measurements were carried out using a four-point-probe apparatus (Quantum Design: PPMS).

III. RESULTS AND DISCUSSION

In Fig. 2 x-ray diffraction (XRD) patterns for the three $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{1-x}\text{Eu}_x)_3\text{Cu}_2\text{O}_{11+\delta}$ samples with $x=0.33, 0.42$, and 0.50 are shown. For $x=0.42$, the diffraction peaks could readily be indexed according to the tetragonal space group $P4/mmm$ (Ref. 17) expected for an ideal (Hg, W)-1232 structure, with lattice parameters, $a = 3.839(3)$ Å and $c = 17.33(2)$ Å. Only trace amounts of impurities, CeO_2 and Sr_2CuWO_6 , are seen for this sample. For the $x=0.33$ sample, the (Hg, W)-1232 phase is still the main phase but the peaks in the XRD pattern due to CeO_2 and Sr_2CuWO_6 have become more prominent. On the other hand,

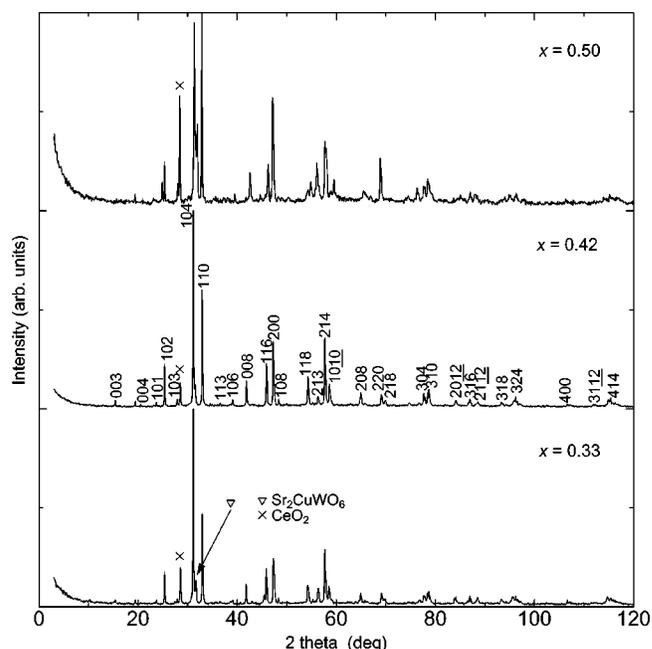


FIG. 2. X-ray diffraction patterns for the $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{1-x}\text{Eu}_x)_3\text{Cu}_2\text{O}_{11+\delta}$ samples with $x=0.33, 0.42$, and 0.50 . The indices given for the most phase-pure $x=0.42$ sample are for the (Hg, W)-1232 structure on the basis of space group $P4/mmm$. Small amounts of CeO_2 and Sr_2CuWO_6 are seen for all samples as an impurity. The $x=0.50$ sample is a mixture of the two copper-oxide phases, (Hg, W)-1232 and (Hg, W)-1222.

rather than the desired (Hg, W)-1232 phase, the $x=0.50$ sample contains the $s=2$ or (Hg, W)-1222 phase as the main phase. Here note that commonly seen for category B-type $\text{MSr}_2(\text{Ce}_{1-x}\text{R}_x)_3\text{Cu}_2\text{O}_{5+2s\pm\delta}$ systems is that the $s=3$ phase is obtained at $x \approx 0.33$ and the $s=2$ phase at $x \approx 0.75$.¹⁸

For the $x=0.42$ sample we further verified the (Hg, W)-1232 crystal structure from an HRTEM image shown in Fig. 3. A perfect layer repetition of $\text{SrO}-(\text{Hg}, \text{W})\text{O}_{1+\delta}-\text{SrO}-\text{CuO}_2-(\text{Ce}, \text{Eu})-\text{O}_2-(\text{Ce}, \text{Eu})-\text{O}_2-(\text{Ce}, \text{Eu})-\text{CuO}_2$ without indication of any stacking faults is clearly discerned from the image. In Fig. 4 shown are ED patterns taken for the same sample with the incident beam along the directions, $[001]$, $[010]$, and $[1-10]$. The ED patterns confirm the findings of the XRD and HRTEM data,

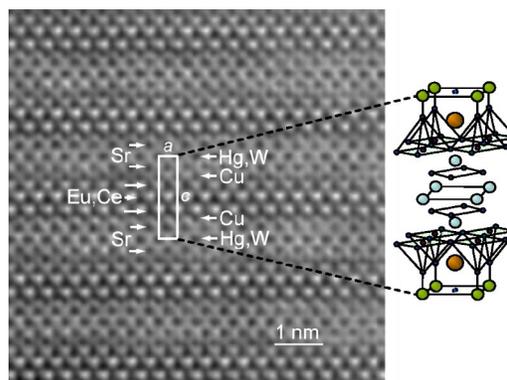


FIG. 3. HRTEM image for the $x=0.42$ sample.

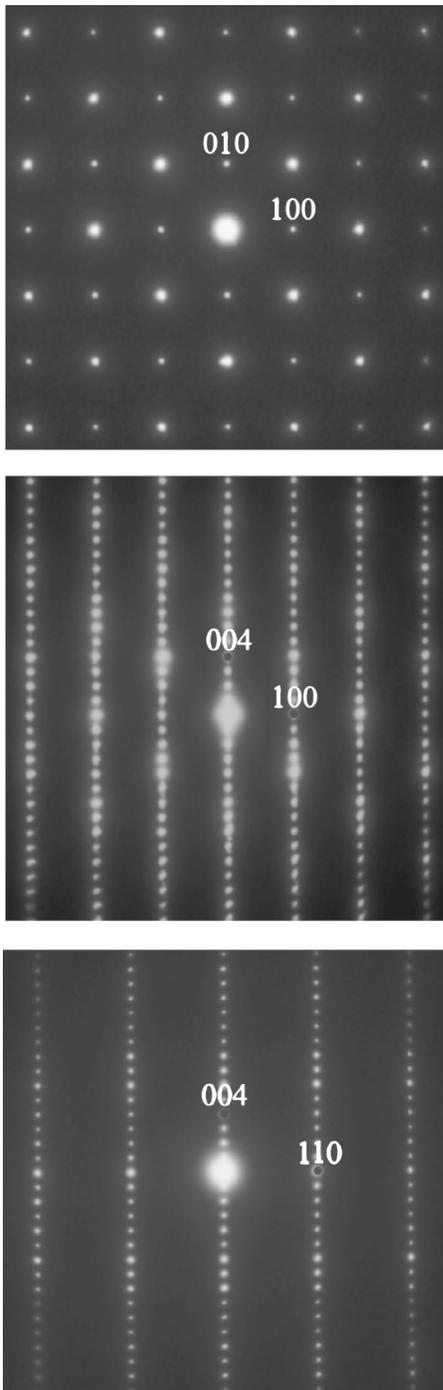


FIG. 4. ED patterns for the $x=0.42$ sample with the incident beam along the directions $[001]$, $[010]$, and $[1-10]$ (from the top to the bottom).

namely a tetragonal lattice with the $a:c$ ratio approximately 1:4. Also the possibility of superstructures was ruled out on the basis of the ED data. From the TEM-EDX analysis data the cation ratios, Hg:W and Ce:Eu, were determined at 0.67:0.33, and 0.56:0.44, respectively, both very close to the corresponding nominal ratios of 0.70:0.30, and 0.58:0.42.

The temperature dependence of magnetization measured in both FC and ZFC modes at 10 Oe for the essentially phase-pure $x=0.42$ sample (Fig. 5) revealed a strong diamag-

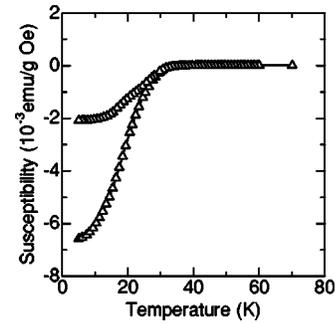


FIG. 5. Temperature dependence of magnetization for the $x=0.42$ sample.

netic signal with the onset temperature at 33 K. The superconducting volume fraction as estimated from the ZFC curve at 5 K is around 59%. Since the two impurity phases, Sr_2CuWO_6 and CeO_2 , seen in trace amounts in the XRD pattern for the $x=0.42$ sample are both nonsuperconductive, we conclude that the large diamagnetic signal detected for this sample is a manifestation of bulk superconductivity of the (Hg,W)-1232 phase. The resistivity (ρ) versus temperature (T) curve for the same sample is shown in Fig. 6. The superconductivity transition is manifested with a clear downturn in resistivity about 30 K. Apparently the quality of grain boundaries in our (Hg,W)-1232 sample is not high. This is rather common for high-pressure-synthesized samples. Accordingly the superconductivity transition behavior superimposes on a semiconductive-type one of the grain boundaries. We therefore determined the superconductivity transition temperature as $d^2\rho/dT^2 \approx 0$ to obtain a value of ~ 34 K that is in good agreement with the value at the diamagnetic onset revealed from the magnetization measurement.

The T_c value of 33–34 K for our as-synthesized $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{0.58}\text{Eu}_{0.42})_3\text{Cu}_2\text{O}_{11+\delta}$ sample of the (Hg,W)-1232 phase is only half of the value reported for the (Hg,W)-1222 phase, i.e., 75 K for $(\text{Hg}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{Ce}_{0.25}\text{Gd}_{0.75})_2\text{Cu}_2\text{O}_z$.^{13,14} However, this does not necessarily mean that an $s=3$ phase would intrinsically have a lower T_c than the corresponding $s=2$ phase. Rather we believe that our as-high-pressure-synthesized $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{0.58}\text{Eu}_{0.42})_3\text{Cu}_2\text{O}_{11+\delta}$ sample is not yet optimized in terms of hole doping. A rough estimate of the valence state of copper is obtained at 2.03 by assuming the ideal stoichiometry of $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{0.58}\text{Eu}_{0.42})_3\text{Cu}_2\text{O}_{11}$

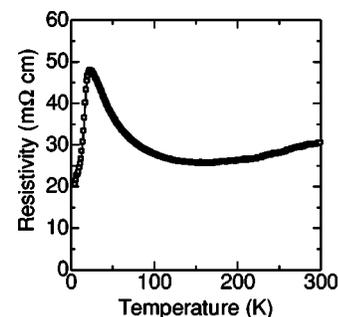


FIG. 6. Temperature dependence of resistivity for the $x=0.42$ sample.

for the (Hg,W)-1232 phase and valence states, +II, +VI, +II, +IV, +III, and -II for Hg, W, Sr, Ce, Eu, and O, respectively. For comparison, a similar calculation for the (Hg,W)-1222 phase using a stoichiometry of $(\text{Hg}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{Ce}_{0.25}\text{Gd}_{0.75})_2\text{Cu}_2\text{O}_9$ reveals a Cu valence value of 2.25. It thus seems that our $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{0.58}\text{Eu}_{0.42})_3\text{Cu}_2\text{O}_{11+\delta}$ sample is in an underdoped state. The fact that the high-pressure synthesis was carried out without an additional oxygen source is in line with this suggestion. The third fact pointing to the same direction is that the T_c values as revealed from magnetization measurements for the other two $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{1-x}\text{Eu}_x)_3\text{Cu}_2\text{O}_{11+\delta}$ samples with $x=0.33$ and 0.50 were 26 K and 45 K, respectively. In other words, it seems that T_c is gradually increased upon increasing the hole-doping level through aliovalent Eu^{III} -for- Ce^{IV} substitution, i.e., $T_c=26$ K ($x=0.33$), 33 K ($x=0.42$), and 45 K ($x=0.50$). Unfortunately the solid-solution range for tuning the Eu/Ce ratio in (Hg,W)-1232 was found rather narrow, and it should be remembered that even the presently employed end stoichiometries of $x=0.33$ and 0.50 yielded multiphase samples. We also made preliminary efforts to introduce more oxygen in the (Hg,W)-1232 phase. However, a postannealing carried out in O_2 gas (at 250°C) did not increase the T_c value but rather decreased it by few degrees, presumably due to some Hg loss. Note that T_c was also found to decrease by

few degrees when postannealing the sample in N_2 (at 250°C). A more systematic study has been initiated on the possibility of increasing the T_c value of the (Hg,W)-1232 phase by controlling the W and Eu contents and/or tuning the oxygen content.

IV. CONCLUSION

In terms of the possible copper-oxide host lattices for the high- T_c superconductivity, we have successfully extended the variety to the 1232-type layered structure in which the CuO_2 planes are separated from each other by a rather thick fluorite-structured $(\text{Ce},R)-\text{O}_2-(\text{Ce},R)-\text{O}_2-(\text{Ce},R)$ block. For our as-synthesized $(\text{Hg}_{0.7}\text{W}_{0.3})\text{Sr}_2(\text{Ce}_{0.58}\text{Eu}_{0.42})_3\text{Cu}_2\text{O}_{11+\delta}$ sample of the three-fluorite-layer (Hg,W)-1232 phase, T_c for bulk superconductivity was found at 33 K. Further optimization of the hole-doping level is apparently required to reach higher T_c values.

ACKNOWLEDGMENTS

This work was supported by Grants-in-aid for Scientific Research (Nos. 15206002 and 15206071) from the Japan Society for the Promotion of Science, and the Nanotechnology Support Project of the MEXT, Japan.

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conductivity in an M -1232 type phase has been claimed or mentioned. However, both the works lack the most crucial experimental evidence required to verify bulk superconductivity of the given phase.

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