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A resistivity anomaly at 380 K in reproduced LK-99

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Abstract

To confirm the room-temperature superconductivity at ambient pressure as claimed in recent arXiv preprints by Lee *et al*., we followed the original authors' systematic solid-state synthesis recipe to reproduce Cu-doped Pb-apatite, known as LK-99. Using X-ray diffraction and Raman spectroscopy, we identified inclusion of various impurities alongside the apatite phase in our sample. While the sample exhibited an overall semiconducting behavior in electrical transport, an intriguing resistivity anomaly at 380 K was observed, possibly originating from a structural phase transition of the $Cu_{2-\delta}S$ impurity. Based on the transport and magnetization measurements, we conclude that the sample is a non-magnetic semiconductor, with absence of superconductivity.

Keywords: room-temperature superconductor, solid-state synthesis, Raman spectroscopy, apatite

1. INTRODUCTION

Since the initial reports by Lee *et al.* [1, 2], suggesting the possibility of superconductivity near 400 K in their $Pb_{10-x}Cu_x(PO_4)_6O$ samples (named LK-99 after the authors), ongoing efforts are being made from all over the globe to test the claim. Although researchers have undertaken efforts to confirm the phenomena in both theory and material synthesis, apart from a few optimistic scenarios from first-principle studies, to our knowledge, none, including the original authors, have yet presented experimental evidence of room-temperature ambient-pressure superconductivity that the scientific community can fully embrace. For example, Hou *et al.* [3] claimed 'zero resistance' in one of their LK-99 samples, exhibiting $R(T < 110\ \text{K})/R(300\ \text{K}) < 10^{-4}$ in electrical transport. However, they also admitted semiconducting behaviors in other samples, similar to those discussed in reference [4] by Liu *et al.*. Guo *et al.* [5] proposed an alternative explanation for the observed half levitation in LK-99 samples, attributing it to ferromagnetism ruling out the Meissner effect. Puphal *et al.* [6] synthesized $Pb_{10-x}Cu_x(PO_4)_6O$ single crystals using the floating zone growth method and demonstrated that the material is a non-magnetic insulator, showing a diamagnetic response up to 800 K. This finding aligns with Kumar *et al.*'s report [7], stating absence of superconductivity in their low impurity polycrystalline samples. Density functional theory (DFT) calculations from several references [8-10] suggest isolated flat bands at the Fermi level due to hybridization of the Cu(3d) and O(2p) orbitals, hopefully related to superconductivity. Also, Oh and Zhang [11] suggested s-wave pairing in their two-band Hubbard model, implying a possibility of low-temperature superconductivity.

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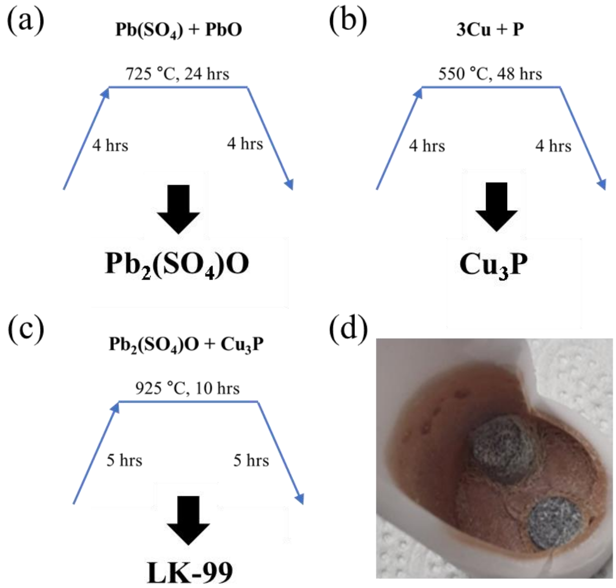

Fig. 1. (a)-(c) Furnace sequences of $Pb_2(SO_4)O$, Cu_3P and LK-99. (d) Photo of synthesized LK-99 samples from (c).

In this report, we followed Lee *et al.*'s recipe of systematic solid-state reaction method [1,2] to synthesize $Pb_{10-x}Cu_x(PO_4)_6O$ samples and measured electrical transport and magnetization in search of room-temperature superconductivity at ambient pressure.

2. EXPERIMENTAL DETAILS

2.1. Precursors synthesis

We followed the procedures outlined by Lee *et al.* [1, 2] to synthesize precursors and LK-99 using a solid-state reaction method. First, we synthesized the precursors,

$Pb_2(SO_4)O$, and Cu_3P. To make $Pb_2(SO_4)O$, we mixed $PbSO_4$ and PbO powders in a 1:1 molar ratio and then compressed them into a pellet under 2 MPa pressure. The resulting pellet was placed in an alumina crucible, sealed in a quartz tube under a vacuum of 10^{-5} torr, and heated at 725 ℃ for 24 hours to synthesize $Pb_2(SO_4)O$ (Fig.1(a)). Similarly, Cu_3P was synthesized by mixing Cu and P in a 3:1 molar ratio, forming a pellet to be sealed in an alumina crucible and heated at 550 ℃ for 48 hours to synthesize Cu_3P (Fig. 1(b)).

2.2. LK-99 synthesis and characterization

After fine grinding the $Pb_2(SO_4)O$ and Cu_3P precursors, the powders were mixed in a 1:1 molar ratio. The mixture was then compressed under 2 MPa pressure to form pellets. These pellets were placed in an alumina crucible, sealed in a quartz tube under a vacuum of less than 10^{-5} torr, and heated at 925 ℃ for 10 hours (Fig. 1(c)). This process resulted in obtaining gray-colored samples as in Fig. 1(d).

To examine the structure and composition of the synthesized LK-99, we employed a high-resolution X-ray diffraction (XRD) analysis with a Cu $K_{\alpha1}$ radiation source using a PANalytical Emperean™ instrument. Additionally, to identify the substances present in LK-99, we conducted room temperature Raman spectroscopy experiments using a Nanobase XperRam200™ spectrometer.

2.3. Electrical transport and magnetization measurements

To confirm the superconducting properties of our synthesized LK-99 samples, we measured their resistivity and magnetization. We determined resistivity using the conventional four-terminal method on a PPMS™ (Quantum Design) apparatus, making electrical contacts on the sample using silver epoxy (Dupont 4929 N). Applying a 1 μA current, we gradually changed the temperature at a rate of 3 K/min. Magnetization was measured using a commercial magnetometer (MPMS™ , Quantum Design) instrument under a magnetic field of 10^4 Oe. The measurements were conducted on a sample with a mass of 66.02 mg, with increasing temperature.

3. RESULTS AND DISCUSSION

First, we characterized the basic properties of the synthesized LK-99 samples. The pristine Pb-apatite possesses a hexagonal lattice structure with the space group P 63/m (No. 176). Fig. 1(a) illustrates a unit cell of $Pb_9Cu(PO_4)_6O$ with lattice constants $a = b = 9.63$ Å and $c = 7.22$ Å. Fig. 2(b) and 2(c) display the room temperature powder XRD results of the LK-99 sample. The XRD patterns reveal more than two distinct phases, suggesting the presence of impurities such as Cu_2S in addition to the apatite phase of LK-99. Due to the overlapping signals, specifying all impurities and determining whether Cu has indeed been doped into the Pb-apatite phase, as claimed by Lee *et al*. [1, 2], proved to be challenging.

Unlike XRD, Raman spectroscopy captures the scattering spectra of a local point on the sample surface. By changing the measurement points for spatial mapping as in Fig. 3(b), it is possible to effectively analyze the composition

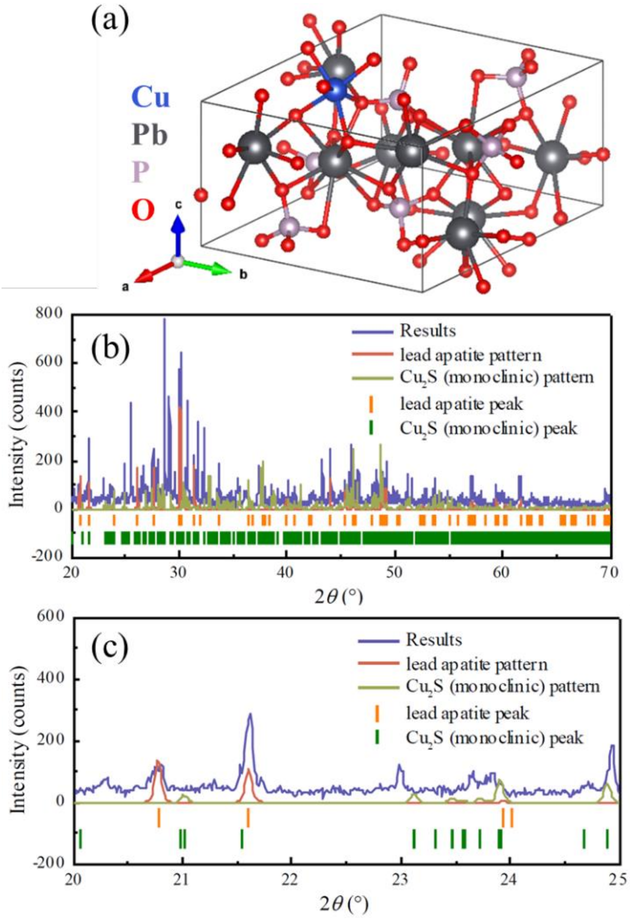

Fig. 2. (a) A unit cell of LK-99. (b) and (c) XRD results of our LK-99 sample.

of the sample. In Fig. 3(a) and 3(c), the Raman scattering signals from the LK-99 sample are identified as $Pb_2(SO_4)O$, $(Pb,Cu)_{10}(PO_4)_6O$, $Cu_3(PO_4)_2$, Cu_3P, Cu_2O_x, and amorphous Cu [14-19]. This supports the presence of multiple impurities within the sample, as evidenced by XRD patterns. Moreover, the identification of impurities other than Cu_2S indicates challenges in achieving a single-phase $(Pb,Cu)_{10}(PO_4)_6O$ using Lee *et al*.'s method [1, 2].

To confirm the possible room-temperature superconductivity of LK-99, we have checked resistivity and magnetization up to 380 K. Fig. 4(a) shows changes in the resistivity of the LK-99 sample with respect to temperature. The red line (blue line) represents the results obtained while increasing (decreasing) the temperature. Overall, the sample exhibits semiconductor-like behavior throughout the temperature range which is in line with Liu *et al.*'s report [4]. There is a hysteresis curve observed between 360 K and 380 K which is likely due to a 1st-order transition. Also, as the temperature decreases, the resistivity increases, indicating that the transition at 380 K is not a superconducting transition and possibly originates from a structural phase transition of $Cu_{2-\delta}S$ [12], as suggested by Puphal *et al*. [6].

Fig. 4(b) shows the temperature-dependent magnetization of the LK-99 sample. The red line (black line) represents the M/H curve while cooling with (without) a 10000 Oe magnetic field and subsequently raising the

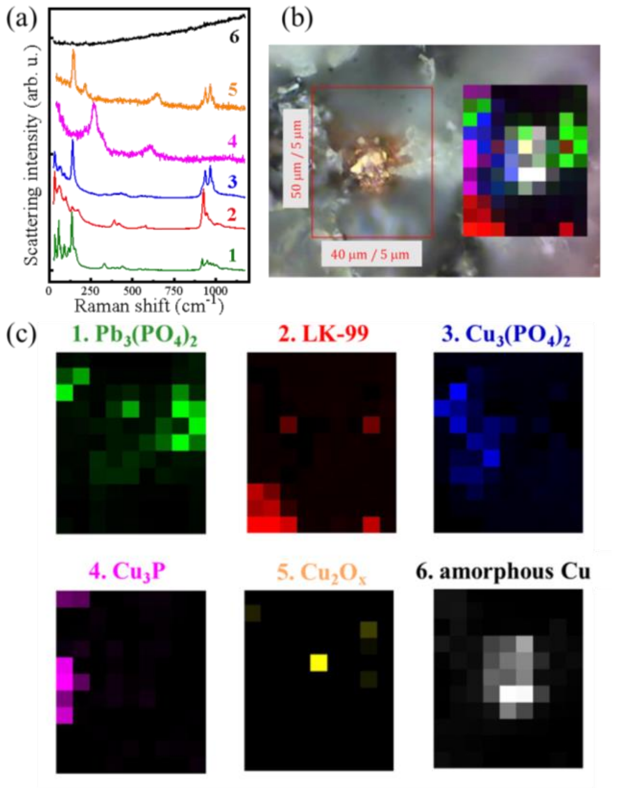

Fig. 3. (a) Raman spectra of the LK-99 sample. (b) Collective of eighty 5 µm × 5 µm local points to map 40 µm × 50 µm region. (c) Spatial mapping results of distinct phases in a LK-99 sample identified as $Pb_2(SO_4)O$, $(Pb,Cu)_{10}(PO_4)_6O$, $Cu_3(PO_4)_2$, Cu_3P, Cu_2O_x, and amorphous Cu.

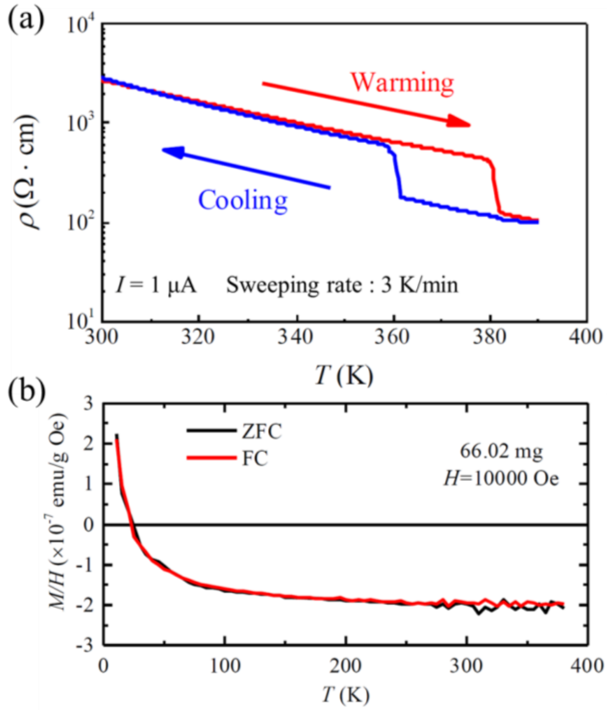

Fig. 4. (a) Resistivity of the LK-99 sample above 300 K. (b) Magnetization of the LK-99 sample under 10000 Oe.

temperature under the magnetic field. The presence or absence of the magnetic field during cooling did not significantly affect the result. The sample exhibited weak diamagnetism (~-2×10^{-7} emu/g·Oe) at room temperature. However, it's important to note that the magnetic susceptibility of a typical diamagnetic material like graphite at room temperature is -2.2×10^{-5} emu/g·Oe [13], which is more than a hundred times greater than that of our LK-99 sample. Given that there is no clear change in magnetization due to a phase transition, we cannot conclude that the room-temperature diamagnetism originates from superconductivity.

4. CONCLUSIONS

In summary, we investigated the synthesis of LK-99 following the initial reports by Lee *et al.* [1, 2]. However, we encountered significant challenges in controlling impurity phases, as evidenced by XRD and Raman scattering measurement results. Although we observed the resistivity anomaly at 380 K, we concluded that this is likely attributed to the structural phase transition of $Cu_{2-\delta}S$ [12]. Magnetization results showed weak diamagnetism at room temperature without any signature of Meissner effect. Overall, we could not observe evidence of superconductivity in our reproduced LK-99 sample.

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