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Synthesis and physical properties of $Pb_{10-x}Cu_x(PO_4)_6O$: A weak diamagnetic material

Yoonseok Han[a], Taehee Lee[a], Junwon Rhie[a], Jaegu Song[a], Seung-Yeop Paek[a], Seokmin Choi[c], Yongmin Kim[d] Sungmin Park[a, b], Hanoh Lee[a, b, *], and Tuson Park [a, b, *]

[a] *Department of Physics, Sungkyunkwan University, Suwon 16419, Republic of Korea*
[b] *Center for Extreme Quantum Matter and Functionality (CeQMF), Sungkyunkwan University, Suwon 16419, Republic of Korea*
[c] *Institute of Basic Science, Sungkyunkwan University, Suwon 16419, Republic of Korea*
[d] *Department of Physics, Dankook University*

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Abstract

Recently, Lee *et al*. claimed that LK-99 is the first room-temperature superconductor at ambient pressure, which quickly captured the attention of both the scientific community and the general public. We tried to replicate $Pb_{10-x}Cu_x(PO_4)_6O$, called as LK-99, and characterized its physical properties by measuring the electrical resistance and Meissner effect. The electrical resistance results for different batches exhibited structural phase transitions at different temperatures, and the magnetic measurements indicated weak diamagnetism at 300 K, which is weaker than that of water. Taken together with the structural analysis, these results suggest that the resistivity transitions are incurred by Cu-S compound generated as a byproduct during the synthesis of LK-99 and LK-99 is not a room-temperature superconductor.

Keywords: LK-99, superconductor, Cu-S

1. INTRODUCTION

Superconductivity, discovered in 1911, has attracted great interest not only because of its scientific merit but also because of its potential applications to modern technologies [1]. This phenomenon represents a macroscopic quantum state that is characterized by zero electrical resistance and perfect diamagnetism (Meissner effects), which has fascinated many scientists. Moreover, when Bednorz and Muller reported an enhanced critical temperature (T_C = 30 K) in $La_{5-x}Ba_xCu_5O_{5(3-y)}$ in 1986 [6], expectations for practical applications soared. This led researchers to devote their efforts with enthusiasm to achieve even higher T_C. The highest T_C obtained at atmospheric pressure was 133 K for $HgBa_2Ca_2Cu_3O_{8+x}$ [2] and for $Hg_{0.8}Pb_{0.2}Ba_2Ca_2Cu_3O_{8+x}$ [7] in 1993. However, the T_C was still too low for most industrial applications. Later in 2019, near-room-temperature superconductivity (T_C above ~250 K) was reported in superhydrides under megabar pressure conditions. While discovering such high T_C superconductors is fascinating, the requirement for extremely high-pressure environments limits their practical appli-cations [3-5].

Recently, the possibly first room-temperature superconductor at ambient pressure, $Pb_{10-x}Cu_x(PO_4)_6O$ (known as LK-99), was reported by S. Lee *et al.* [8, 9], where an abrupt drop in resistivity was observed below ~ 380 K with a corresponding diamagnetic response. Not only the scientific community, but also the general public in the world were excited about the news owing to the outstanding potential of room temperature superconductor to revolutionize the energy and technology systems. Materials synthesized through the reported synthesis method by S. Lee *et al*., however, observed significantly different results with no superconductivity [10-32], leading numerous scientists to raise questions about the nature of LK-99.

In this article, we report synthesis of the proposed room-temperature superconductor $Pb_{10-x}Cu_x(PO_4)_6O$, where we followed the reported synthesis method by S. Lee *et al.* [8, 9] and measured corresponding physical properties. The X-ray diffraction (XRD) peaks of crystals matched the expected ones for LK-99 with additional impurities including, Cu, Cu_2S, and $Pb_4P_2SO_{12}$. However, the electrical resistance is failed to reach zero, indicating that LK-99 is not a room temperature superconductor.

2. EXPERIMENTAL DETAILS

Lanarkite ($Pb_2(SO_4)O$) was synthesized by mixing PbO (Thermos Scientific, 99.9 % powder) and $PbSO_4$ (Alfa Aesar reagent grade, powder) in a 1 : 1 compositional ratio in a mortar and pressing them into a pellet form. The pellets, then, were placed in an alumina crucible, heat treated at 725 °C for 24 hours, and naturally cooled in an electric furnace. As for Cu_3P precursor, Cu (Alfa Aesar, powder, 99.9 %) and P (Red phosphorus, Alfa Aesar, 99.999 %) were mixed in a mortar in a glove box under an argon environment with a compositional ratio of 3 : 1.1. Then, the Cu-P mixture were sealed in quartz tubes under 1×10^{-3} torr and annealed in electric furnace at 550 °C for 48 hours.

* Corresponding author: hlee.rtf@gmail.com, tp8701@skku.edu

Three batches of $Pb_{10-x}Cu_x(PO_4)_6O$ were synthesized by the thermal annealing technique, where $Pb_2(SO_4)O$ and Cu_3P with 1 : 1 ratio were sealed in quartz ampoules under vacuum condition. The ampoules were heat treated at 925 ^oC for 10, 10, and 24 hours, respectively, followed by natural cooling in the furnace for batch 1 and 3, while batch 2 was cooled to room temperature at a rate of 100 ^oC/hour. The resulting samples have dark gray colors with copperish spots and pink colors at the outer surface area.

The crystal structure of the synthesized $Pb_2(SO_4)O$, Cu_3P, and $Pb_{10-x}Cu_x(PO_4)_6O$ was investigated using an X-ray diffractometer (Rigaku miniflex-600 diffractometer, Cu-$K_{\alpha1}$ radiation, $\lambda = 1.541$ Å). The morphology image of Batch 3 and stoichiometries of $Pb_{10-x}Cu_x(PO_4)_6O$ were obtained using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. The electrical resistance and magnetism of $Pb_{10-x}Cu_x(PO_4)_6O$ were measured using closed cycle refrigerator (CCR) with AC-Resistance bridge (Lakeshore, LS370) and magnetic property measurement system (MPMS, Quantum Design), respectively.

3. RESULT AND DISCUSSION

The X-ray diffraction (XRD) results of $\theta - 2\theta$ scan of Cu_3P and Lanarkite were shown in Fig. 1 (a) and (b), respectively. The XRD patterns of Cu_3P and Lanarkite are consistent with the hexagonal crystal structure (space group $P6_3/m$, 176). The corresponding lattice parameters, analyzed by FullProf software, are a = 6.9654 Å, c = 7.1417 Å for Cu_3P and a = 9.8793 Å, c = 7.2735 Å for Lanarkite. Figure 1(c) and (d) show the XRD pattern of $Pb_{10-x}Cu_x(PO_4)_6O$ from the batch 2 and 3, respectively, where the calculated peaks expected for LK-99 are similar to the reports by S. Lee *et al.* [8, 9].

Additional peaks that were not identified are from impurity phases. In batch 1 (not shown), strong Cu peaks appear from the excessive amount of Cu, while the Cu content is less for the batch 2 and 3. In addition, all the batches show obvious peaks from $Pb_4P_2SO_{12}$ and Cu_2S

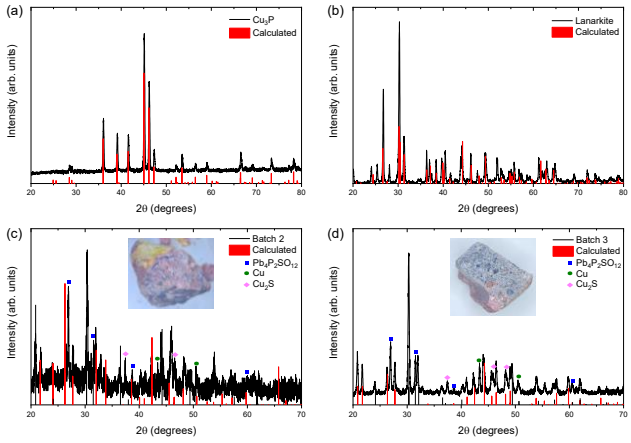

Fig. 1. X-ray diffraction (XRD) patterns for (a) Cu_3P, (b) Lanarkite, (c) batch 2, and (d) batch 3. Red line represents the XRD results calculated with FullProf software.

TABLE. 1
SUMMARY OF SYNTHESIS METHOD AND XRD ANALYSIS RESULTS OF $Pb_{10-x}Cu_x(PO_4)_6O$ AS A FUNCTION OF t_a AND Cu_3P : $Pb_2(SO_4)O$ RATIO. THE LATTICE PARAMETER a AND c OF BATCH 1, 2, AND 3 WERE CALCULATED FROM XRD PATTERNS.

	t_a (h)	Cu_3P : $Pb_2(SO_4)O$	a (Å)	c (Å)	Cu_2S
LK-99 [7, 8]	5 ~ 20	1 : 1	9.843	7.428	○
Batch 1	10	1 : 1	9.836	7.328	○
Batch 2	10	1 : 1	9.825	7.370	○
Batch 3	24	0.9 : 1	9.825	7.631	○

impurities. The XRD for the pink area also shows overall comparable peak patterns to that of the gray area, suggesting that they may share similar crystal structure to that of LK-99 although the electrical resistance of the pinky parts was very high and not in the measurable range with our resistance bridge, unlike the gray colored area where the temperature dependent resistance was measured and discussed in Fig. 2. Energy Dispersive X-ray Spectroscopy (EDS) analysis on the samples shows similar results with the XRD analysis, where lead apatite with various copper content (~ 5-20%) were detected (data not shown). The impurity phases of Cu, $Pb_4P_2SO_{12}$, Cu_2S were also observed in the EDS analysis.

Table 1 presents a comparison of lattice parameters and impurity phases between the previously reported LK-99 [8, 9] and our results. The calculated lattice parameters of $Pb_{10-x}Cu_x(PO_4)_6O$ are a = 9.836 Å and c = 7.328 Å for batch 1, and a = 9.825 Å and c = 7.370 Å for batch 2. The lattice parameter for batch 3, where the Cu_3P was reduced by 10 % and the annealing time (t_a) was extended to 24 hours, are a = 9.825 Å and c = 7.631 Å. In addition to the LK-99 phase, Cu_2S impurities was identified in all batches. The overall lattice constants are smaller than that of lead apatite and comparable to the reported LK-99 case. We note that the lattice constants may not be accurately estimated because the doping level appears to be fluctuating within each batch.

Figure 2 (a) shows morphology of Batch 3 by SEM image. The corresponding chemical compositions of the samples reveal the presence of multiple impurity phases coexisting with LK99-like phases. Cu content also varies from 3 to 13% even within a single specimen. Additionally, silicon inclusions have been detected, suggesting partial replacement of P-sites, most likely due to the reactions with the quartz tube during heat treatment. The estimated stoichiometries of LK-99 like phase with the gray part of the samples for batches 1, 2, and 3 are $Pb_{9.34}Cu_{0.64}P_{4.44}O_{20.10}Si_{1.37}$, $Pb_{9.68}Cu_{0.31}P_{5.02}O_{27.59}Si_{0.56}$, and $Pb_{8.81}Cu_{1.19}P_{4.93}O_{18.04}Si_{1.18}$, respectively. The stoichiometry of the red part in batch 2 is $Pb_{6.23}Cu_{3.77}P_{2.58}O_{33.63}Si_{3.67}$. Notably, the red part of the sample exhibits high concentrations of silicon and copper compared to the gray part, possibly due to a more pronounced reaction with the quartz tube and copper during the annealing process. Figure 2 (b)-(d) show the temperature dependence of the electrical resistance for the samples from the gray area of the batches 1, 2, and 3 (see the inset of Fig. 1). The

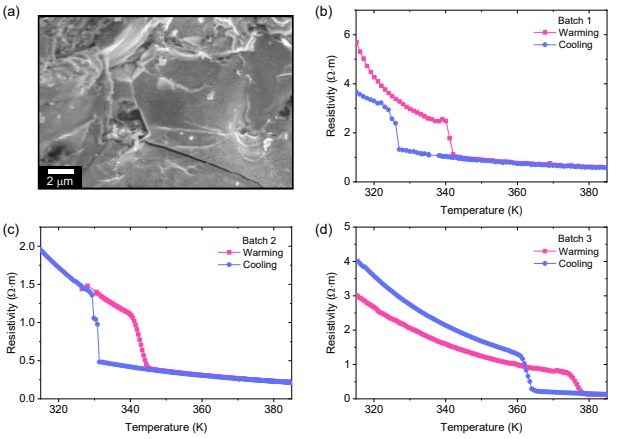

Fig. 2. (a) shows a morphological SEM image for Batch 3. Temperature dependence of the electrical resistivity (ρ) for (b) batch 1, (c) 2, and (d) 3. Resistance results shows different transition temperature while increasing and decreasing temperature in measurements.

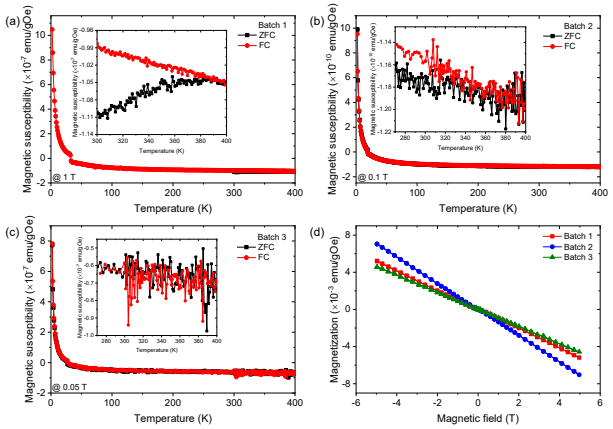

Fig. 3. Temperature dependence of magnetic susceptibility for (a) batch 1, (b) 2, and (c) 3. The field-cooled (FC) and zero-field-cooled (ZFC) of batch 1, 2, and 3 were measured at 1, 0.1, and 0.05 Tesla, respectively. (d) Magnetic field-magnetization (*M*-*H*) curve of batch 1, 2, and 3 at 200 K.

measurements were conducted over the temperature range between 310 K and 390 K, employing continuous warm-up and cooling-down cycles. In contrast to the anticipated superconducting electrical resistance behavior [1], the samples from all three batches exhibit an overall insulator-like feature. In addition, abnormal transitions were observed in batches 1, 2, and 3 within the temperature ranges of 320−340 K, 330−345 K, and 360−380 K, respectively. The transition at approximately 360−380 K in batch 3, characterized by a resistivity jump, aligns with findings from other studies, where the jump has been attributed to the presence of a small amount of Cu_2S inclusion as an impurity [24, 30]. Our XRD as well as the EDS results show the existence of the Cu_2S phase in all three batches, supporting the scenario that this transition is related to Cu_2S inclusion. The features in batch 1 and 2, on the other hand, occur at lower temperature than those associated with Cu_2S and do not correspond with any reported transitions for LK-99 related materials. One possible explanation could be a slight off-stoichiometry between Cu and S in Cu_2S phase, i.e. $Cu_{2-x}S$, where thermal hysteresis is influenced by increasing x and appears down to ~300 K for x = 0.2 [34]. We note, however, that the presence of multiple impurity phases in our samples, along with varying Cu-content, makes it difficult to determine the origin of these transitions observed below ~340K.

The magnetic response of these same pieces were too small to probe using our equipment. Therefore, larger pieces from the same batches were measured to identify the magnetic properties. Figure 3 (a)-(c) show the magnetic susceptibility (*M*/*H*) as a function of the temperature for batch 1, 2, and 3, respectively, where black squares and red circles represent the zero-field-cooled (ZFC) and field-cooled (FC) measurements from 400 to 2 K. The *M*/*H* data show weak diamagnetic properties from 33 K to 400 K for all three batches with the values of -1.101×10^{-7}, -1.170×10^{-10}, and -6.405×10^{-8} emu/gOe at 300 K for batch 1, 2, and 3, respectively. These diamagnetic signals are much smaller than that of water (-0.505×10^{-4} emu/gOe). Small difference between ZFC and FC curves is observed, as shown in the insets of (a) and (b), which could be related to the transitions observed in the resistance curves. The deviation temperatures between ZFC and FC measurements differ from the corresponding transition temperatures observed in the resistivity, which may be due to the sample dependency with different impurity levels. Figure 3(d) displays the magnetic field dependence of the magnetization (*M*) for all three samples. The negative linear in magnetic field dependent signals for all the magnetization curves reveal again small diamagnetic signal, which is consistent with the temperature dependent *M*/*H* values. We note that there are no superconducting-like features in the *M* versus *H* curves.

To summarize, we synthesized LK-99 ($Pb_{10-x}Cu_x(PO_4)_6O$) following the instructions by S. Lee *et al.* and investigated the physical properties as a function of the temperature and magnetic field. XRD analysis showed similar peaks corresponding to those expected from LK-99. EDS analysis indicates additional inclusion of Si in our samples. Electrical resistivity and magnetic property results, however fail to evidence any hints of superconducting characteristics, but rather reveal an insulating behavior. These results suggest that LK-99 is not likely a superconductor, but its electrical transport and magnetic properties seem to be related to the Cu-S impurity phase.

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