SPECIAL TOPIC — John Tse: Pioneer in high-pressure materials science

Cu1234 single crystals growth with contamination-free quality

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(Received 6 January 2026; revised manuscript received 2 March 2026; accepted manuscript online 4 March 2026)

The $CuBa_2Ca_3Cu_4O_{10+\delta}$ (Cu1234) superconductor exhibits a unique combination of high critical temperature (118 K ambient T_c), high critical current density (J_c), and high irreversibility field (H_{irr}), i.e. the so-called triple-high attributes, making it a promising candidate for high-temperature and high-field applications. However, the growth of high-quality single crystals has been hindered by contamination from traditional sample capsules used in conventional high-pressure synthesis, leading to suppressed T_c. In this work, we develop a modified high-pressure sample assembly utilizing a capsule with MgO as the inner layer and Pt as the outer layer, which effectively prevents undesirable doping of Pt into Cu1234 that suppresses T_c. This approach enables the successful growth of Cu1234 single crystals with a sharp superconducting transition at $T_c \sim 115$ K, comparable to that of polycrystalline samples. Structural and compositional analyses confirm the phase purity, strong *c*-axis orientation, and near-ideal stoichiometry close to the Cu1234 formula. These high-quality Cu1234 single crystals provide a reliable platform for elucidating the intrinsic mechanisms of the exceptional triple-high superconducting properties of the Cu1234 system.

Keywords: Cu1234 superconductor, crystal growth, high-pressure synthesis

PACS: 74.72.−h, 74.25.−q, 74.62.Bf, 81.10.−h

DOI: 10.1088/1674-1056/ae4d28 **CSTR:** 32038.14.CPB.ae4d28

1. Introduction

Cuprate superconductors are currently the only materials known to achieve superconductivity above liquid nitrogen's boiling temperature at ambient pressure,[1–4] making them the exclusive platform for high temperature superconducting applications.[5–7] The $CuBa_2Ca_3Cu_4O_{10+\delta}$ (Cu1234) superconductor has long attracted extensive research interest due to its relatively high T_c (~ 118 K) combined with low crystallographic anisotropy and the absence of toxic elements.[8–13] Especially, the Cu1234 superconductor exhibits an H_{irr} (~ 21 T) and a high J_c ($\sim 5\times10^5$ A/cm^2) at 77 K,[14] which is considered comparable to the widely used $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductors in comprehensive performance. Owing to these distinct triple-high properties — high T_c, high J_c, and high H_{irr} — the Cu1234 superconductor demonstrates considerable potential for future high-temperature and high-field applications. Recently, significant efforts have been directed toward fabricating Cu1234 in wire or tape form through various processing routes,[15,16] aiming to enable its practical use in areas such as superconducting power transmission, high-field magnets, and magnetic levitation systems.

To elucidate the origin of the superior superconducting properties in Cu1234, it is instructive to compare its crystal structure with that of YBCO and other cuprate superconductors. Figure 1(a) illustrates the crystal structure of Cu1234, which consists of superconducting layers [$Ca_3Cu_4O_8$] (SCL) comprising four [CuO_2] planes and perovskite-type charge reservoir blocks [$BaCuO_{3-\delta}$] (CRB), whereas Fig. 1(b) shows the structure of YBCO. Unlike Tl- or Hg-based cuprate superconductors, whose charge reservoirs exhibit a rock-salt configuration resulting in weak interlayer coupling and a significant drop in J_c with increasing temperature, the CRB of both Cu1234 and YBCO adopts a perovskite-like structure. In this structure, the conducting Cu–O chains connect through apical oxygens and have strong interlayer coupling. This coupling effectively enhances the magnetic flux pinning strength, significantly improving the dependence of J_c on temperature and magnetic field.[17] Consequently, Cu1234 exhibits excellent characteristics even under high-temperature and high-field conditions. Moreover, structural comparison reveals that YBCO shares the same basic architecture as Cu1212 (the $n=2$ member of the Cu-based homologous series). This structural identity explains why Cu1234 inherits the low anisotropy and superior J_c behavior characteristic of YBCO, while further enhancing T_c through its multi-layered [CuO_2] planes.

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The preceding analysis elucidates the structural origins of the triple-high characteristics in Cu1234. Nevertheless, the intrinsic physical mechanisms responsible for these properties remain unclear. Elucidating the origin of the exceptional performance in Cu1234 superconductors is crucial for guiding the rational design and synthesis of new high-performance superconductors. High-quality Cu1234 single crystals provide an ideal platform for probing the fundamental mechanisms underlying these triple-high superconducting properties. However, previous studies have reported that the T_c of Cu1234 single crystals ranges from 68 K to 111 K, significantly lower than the value of 118 K observed in polycrystalline samples.[18–20] It is therefore imperative to identify the causes of T_c suppression in single crystals and to improve experimental methods for growing single crystals with T_c comparable to that of polycrystalline specimens. In homologous superconductors such as Cu1223 and Cu1245, T_c can be effectively tuned by adjusting the oxygen content through annealing.[21,22] Thus, one plausible explanation for the lower T_c in Cu1234 single crystals could be insufficient carrier concentration due to oxygen deficiency. However, post-annealing studies on Cu1234 have shown that its T_c varies only slightly from 118 K to 114 K with changes in oxygen content — a range still higher than the T_c observed in single crystals.[23] This indicates that oxygen content alone cannot account for the suppressed T_c in Cu1234 single crystals. Tokiwa *et al*. suggested that chemical contamination from the synthesis environment is the most likely cause of the T_c reduction.[19] They found that during high-pressure synthesis, Au impurities from the capsule can diffuse into the sample and substitute for Cu sites in the CRB of Cu1234, leading to a linear decrease in T_c with increasing Au content.[19]

Based on the preceding discussion, it is essential to grow Cu1234 single crystals free of gold contamination in order to elucidate their intrinsic superconducting mechanisms. In this work, we designed a special sample assembly to suppress Au diffusion during high-pressure synthesis, thereby enabling the successful growth of high-quality Cu1234 single crystals. Magnetization measurements reveal a T_c of approximately 115 K in these crystals, comparable to that of polycrystalline samples. The maximum crystal dimensions obtained are approximately $300 \times 200 \times 20$ μm^3. Energy-dispersive x-ray spectroscopy (EDS) analysis confirms a chemical composition of Ba:Ca:Cu:O = 2 : 3 : 4.54 : 10.16, which nearly aligns with the ideal stoichiometry of the Cu1234 superconductor. The successful growth of these high-quality single crystals provides a reliable platform for investigating the intrinsic mechanisms underlying the outstanding properties of the Cu1234 superconductor.

2. Experiment details

Cu1234 single crystals were synthesized under high-pressure and high-temperature conditions in two steps.[8] First, the $BaCuO_2$ and Ca_2CuO_3 precursors were prepared by a solid-state reaction. The precursor $BaCuO_2$ was prepared by calcining a mixture of BaO_2 (95% pure, Alfa Aesar) and CuO (99.995% pure, Alfa Aesar) at 900 °C for 40 h in air with several intermediate grindings. Ca_2CuO_3 was prepared by calcining a mixture of CaO (99.99%, Alfa Aesar) and CuO at 1000 °C for 20 h in air. Then, the $BaCuO_2$, Ca_2CuO_3, and CuO were mixed to the nominal composition Ba:Ca:Cu = 2 : 3 : 5. AgO was added as an oxidizer, and a mixture of $BaCuO_2$ and CuO was used as the flux. The powders were well-ground and pressed into a pellet, which was then sealed into our designed assembly. All preparation procedures were performed in a glove box under an Ar atmosphere due to the highly hygroscopic nature of alkaline-earth metal oxides. The Cu1234 single crystals were grown using a high-pressure cubic anvil apparatus by the flux method. After the pressure was gradually increased to 5 GPa, the sample was heated to 1250 °C and maintained for 4 h.[10] Then, the temperature was reduced to ambient conditions before releasing the pressure. Sizable single crystals were manually isolated from the crushed bulk sample under an optical microscope. X-ray diffraction (XRD) was conducted at room temperature using an N3 PhiniX X-ray diffractometer with Cu K_α radiation at an operating voltage and current of about 40 kV and 30 mA, respectively. The chemical composition of the single crystal samples was determined by energy-dispersive x-ray spectroscopy (EDS) in a ZEM18 scanning electron microscope (SEM). The magnetic properties were measured using a Quantum Design MPMS3 system in direct current (DC) mode.

3. Results and discussion

In conventional high-pressure synthesis, precious metals such as platinum (Pt) and gold (Au) are commonly employed as sample containers due to their chemical stability under extreme conditions (e.g., high-pressure and high-temperature environments) and their inertness toward precursor materials. Because Au is known to diffuse into the sample and contaminate Cu1234 single crystals,[19] we initially selected a Pt capsule as the sample container. The initial sample assembly, illustrated in Fig. 2(a), allowed direct contact between the sample and the Pt capsule. However, at the temperatures required for single-crystal growth (typically > 1200 °C), Pt tends to react with the sample. XRD analysis revealed the presence of the Ca_4PtO_6 phase, indicating that the Pt capsule reacted with the raw materials at high temperature, thereby impeding crystal growth. To overcome this issue, we designed a modified assembly, shown in Fig. 2(b), in which the sample was

first loaded into a MgO inner capsule and then sealed within a Pt outer capsule. This configuration physically separates the sample from the Pt capsule via the MgO barrier, preventing direct reaction between them. With this design, we effectively suppressed the reaction between Pt and the sample and ultimately obtained high-quality Cu1234 single crystals.

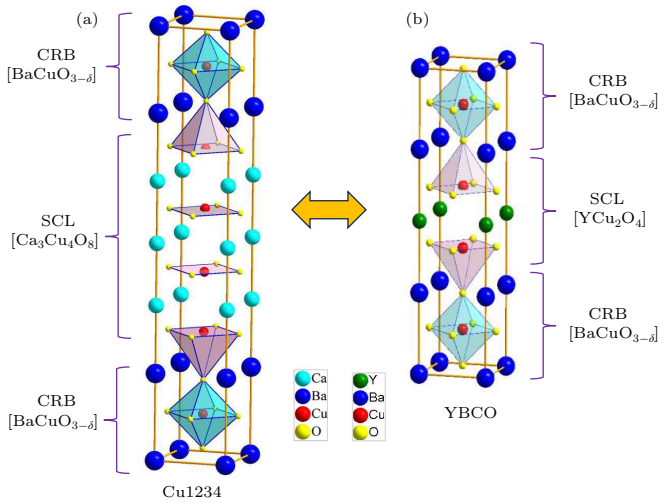

Fig. 1. Crystal structure comparison between (a) $CuBa_2Ca_3Cu_4O_{10+\delta}$ and (b) $YBa_2Cu_3O_{7-\delta}$. Both structures contain $[BaCuO_{3-\delta}]$ perovskite-type charge reservoir blocks (CRB) and superconducting layers (SCL) comprising multilayer $[CuO_2]$ planes.

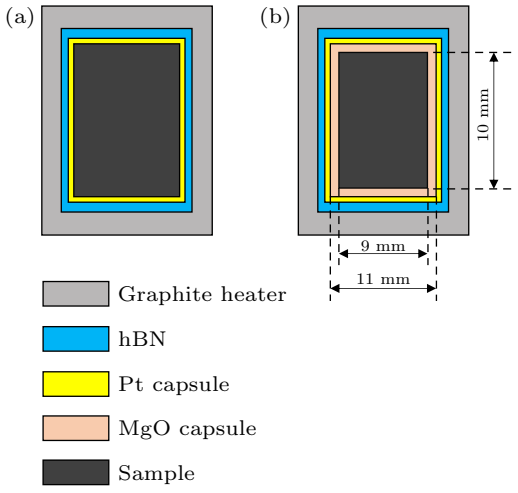

Fig. 2. Two types of sample assemblies for Cu1234 single-crystal growth under high pressure.

We performed XRD analysis on a sheet-like Cu1234 single crystal. As shown in Fig. 3(a), the obtained XRD pattern exhibits exclusively sharp (00l) reflections, demonstrating a highly oriented crystal structure along the c-axis. The absence of any impurity peaks or reflections from other crystallographic directions confirms the high crystalline purity of the sample. Based on the angular positions of the (00l) diffraction peaks, the c-axis lattice parameter was calculated to be $c = 17.955$ Å, which aligns well with previously reported values for the Cu1234 phase (typically in the range of 17.9 ∼ 18.0 Å), thus structurally verifying the successful synthesis of the target phase. Furthermore, the narrow full width at half maximum (FWHM) values of the diffraction peaks indicate excellent crystalline quality and strong c-axis orientation of the grown single crystal. Figure 3(b) displays the temperature dependence of the magnetic susceptibility (χ) for the same Cu1234 single crystal, measured under an external field of 10 Oe in both zero-field-cooled (ZFC) and field-cooled (FC) modes. The χ–T curves exhibit a sharp superconducting transition with a $T_c^{onset} \sim 115$ K. The shielding volume fraction at 30 K is estimated to be 185%, a value which can be attributed to a significant demagnetization effect resulting from the irregular morphology of the crystal. It is noteworthy that the T_c of the obtained single crystal is comparable to that reported for Cu1234 polycrystalline samples. These results collectively confirm that the specially designed assembly enabled the successful growth of high-quality Cu1234 single crystals.

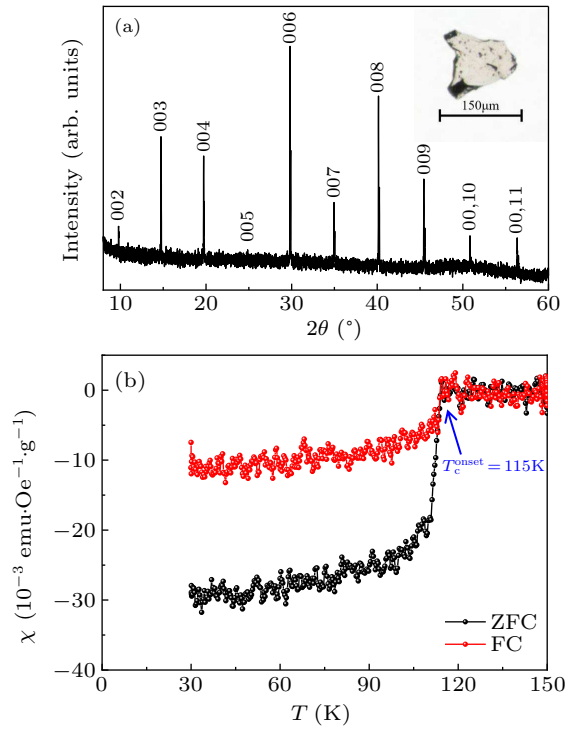

Fig. 3. (a) XRD pattern of the Cu1234 single crystal. Inset shows a photograph of the Cu1234 single crystal. (b) Temperature dependence of magnetic susceptibility for the same Cu1234 single crystal measured in ZFC and FC modes under an external magnetic field of 10 Oe.

To further analyze the composition of the single crystals, we performed SEM coupled with EDS. The inset of Fig. 4 shows the SEM image of a Cu1234 single crystal, exhibiting a notably flat surface. The typical size of separable crystals was about 100 μm in the in-plane direction and 5 μm in thickness, while the largest crystal obtained measured approximately $300 \times 200 \times 20$ μm^3. However, larger crystals were difficult to isolate from the bulk sample. The chemical composition of the crystal was examined by EDS, and a representative EDS spectrum is displayed in Fig. 4. To obtain accurate composition data for the Cu1234 single crystal and minimize errors associated with single-point mea-

surements, EDS analysis was performed at five distinct locations marked by crosses in the SEM image. The results are summarized in Table 1. By averaging EDS data collected from several random locations on the crystal and normalizing the Ba content to 2, the atomic ratio was determined to be Ba:Ca:Cu:O = 2 : 3 : 4.54 : 10.16. This corresponds to a nominal formula of $Cu_{0.54}Ba_2Ca_3Cu_4O_{10.16}$, indicating copper deficiency in the Cu1234 single crystal. The result aligns with previous TEM observations reporting substantial copper deficiency in the CRB of Cu1234 superconductor.[17] Although EDS quantification of light elements such as oxygen is subject to uncertainty, the cation ratios provide strong evidence for the formation of the target Cu1234 single crystal.

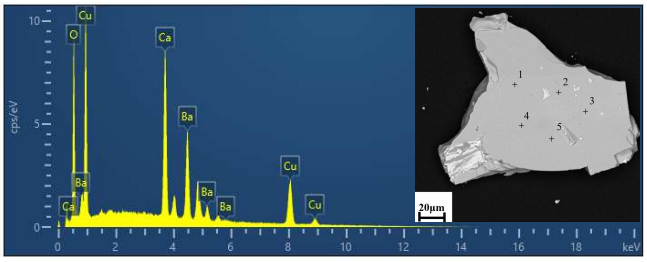

Fig. 4. A typical SEM-EDS spectrum of the Cu1234 single crystal.

Table 1. Chemical compositions of the Cu1234 single crystal examined by EDS measurements.

Element	Atomic concentration (%)					
	Pos. 1	Pos. 2	Pos. 3	Pos. 4	Pos. 5	Average
O	51.62	51.32	51.72	51.91	51.40	51.59
Cu	22.89	23.14	22.82	22.87	23.27	23.00
Ca	15.31	15.37	15.30	15.22	15.12	15.26
Ba	10.18	10.17	10.16	10.01	10.22	10.15

4. Conclusion

In summary, we have developed a modified sample assembly using an MgO-lined Pt capsule to effectively eliminate Pt contamination during the high-pressure growth of Cu1234 single crystals. This approach successfully yields high-quality, *c*-axis-oriented single crystals with a $T_c \sim 115$ K, which closely matches that of polycrystalline samples. Structural and compositional characterizations confirm phase purity, near-ideal stoichiometry, and slight Cu deficiency consistent with previous reports. The obtained crystals not only resolve the long-standing issue of T_c suppression in single-crystal form but also establish a reliable material platform for probing the intrinsic mechanisms underlying the exceptional triple-high properties of Cu1234. This work provides a feasible synthesis route and fundamental insights that can facilitate the further development and practical application of this promising high-temperature superconductor.

Acknowledgments

This work was supported by the Chinese Academy of Sciences Superconducting Research Project (Grant No. SCZX-0101), the National Natural Science Foundation of China (Grant No. 12204515), the National Key Research and Development Program of China (Grant Nos. 2022YFA1403800, 2023YFA1406000, and 2024YFA1408000), the Beijing Natural Science Foundation (Grant No. 1262041), and the Young Elite Scientists Sponsorship Program of China Association for Science and Technology (Grant No. 2022QNRC001).

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