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Synthesis and Characterization of the Superconducting Compound $\text{HgBa}_2\text{CuO}_{4+x}$

Nam Hwi Hur*, In Seon Kim, Yong Ki Park,
and Jong Chul Park

*Korea Research Institute of Standards and
Science, Taejeon 305-606*

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Recently Schilling *et al.*¹ reported the rise of the superconducting critical temperature up to 134 K in the Hg-Ba-Ca-Cu-O system, shortly after the discovery of superconductivity at 94 K in $\text{HgBa}_2\text{CuO}_{4+x}$ by Putlin *et al.*² The observation of superconductivity on the novel mercury-based cuprate oxides has generated great interests in the fields of superconductivity³⁻⁵. In addition to their remarkable high critical transition temperature, the mercury compounds are attractive because of the structural similarity with the thallium based compounds such as $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$. The possible homologous series of single HgO layered $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ ($n=1, 2, 3$) compounds were thus expected to be synthesized with use of analogous preparative techniques. Due to decomposition of HgO at 500°C and sensitiveness to the moisture in the product, isolation of single phasic mercury based cuprate is difficult. In this communication we report the successful isolation of pure superconducting $\text{HgBa}_2\text{CuO}_{4+x}$ by using precursor method.

The bulk samples were prepared by solid state reaction between yellow HgO (Janssen Chimica, 99%) and precursor powders of $\text{Ba}_2\text{CuO}_{3+x}$. A precursor material $\text{Ba}_2\text{CuO}_{3+x}$ was obtained from the reaction of stoichiometric mixtures of BaO_2 (Kanto Chemical Co., 90%) and CuO (Aldrich, 99%) in an oxygen atmosphere for 20 h at 900°C. Immediately after sintering, the pellets of the $\text{Ba}_2\text{CuO}_{3+x}$ were brought into the argon-filled dry box to avoid the decomposition of the compound in air. The precursor powder was mixed with slight excess (1.1 to 1.2 fold) of HgO, compacted into pellets, and finally sealed in evacuated quartz tubes. All these operations were performed in the dry box. The sealed quartz tube was placed inside a steel container which was kept in a bottom

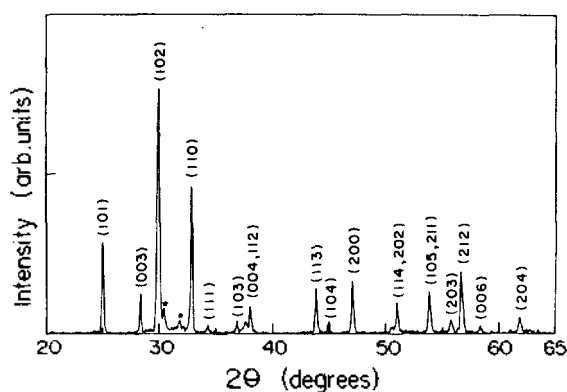


Figure 1. X-ray powder diffraction pattern of $\text{HgBa}_2\text{CuO}_{4+x}$ compound.

loading furnace to prevent contamination of mercury by exploding the silica tubes during the reaction period. The samples were heated slowly to 800°C in 6 h, sintered at the temperature for 5 h, and then slowly cooled to room temperature in 10 h. During the reaction period the quartz tube remained intact. The black pellets were obtained along with a drop of mercury inside the tube.

Attempts to synthesize the $\text{HgBa}_2\text{CuO}_{4+x}$ compound with use of individual metal oxides led to non-superconducting product. This suggests that the reaction between the individual oxides requires higher temperature to form the superconducting phases. In order to make the $\text{HgBa}_2\text{CuO}_{4+x}$ compound, we used $\text{Ba}_2\text{CuO}_{3+x}$ as a precursor material and slight excess amount of HgO to compensate evaporation of mercury in this study. Synthesis of pure $\text{HgBa}_2\text{CuO}_{4+x}$ was strongly dependent on experimental conditions such as reaction rate, sintering temperature, and moisture. The products prepared by similar preparative conditions often gave non-superconducting compounds. Minimum exposure in air and fully dried starting materials could avoid the formation of undesirable side products. $\text{HgBa}_2\text{CuO}_{4+x}$ phase was revealed by X-ray powder diffraction as shown in Figure 1. All the diffraction lines are well indexed on a tetragonal cell ($P4/mmm$) with lattice parameters, a and c with the value of 3.8868 (2) Å and 9.4886 (1) Å, respectively. Trace amounts of unreacted HgO peaks were identified, which were marked asterisks. Pure single phasic $\text{HgBa}_2\text{CuO}_{4+x}$ was obtained by controlling HgO amount, where optimum amount of HgO in this reaction is about 1.1 fold excess. The finely ground powder samples used for X-ray measurement were stable in air for one day but appeared to decompose slowly into greenish black powders. The structure of $\text{HgBa}_2\text{CuO}_{4+x}$ is very similar with the known $\text{TlBa}_2\text{CuO}_{5-x}$,⁶ besides the oxygen contents in rock-salt layers of HgO_x and TlO_{1-x} . While the oxygen in the HgO layer is largely depleted (x is about 0.10)¹, corresponding TlO layer shows very small amount of oxygen-deficiency.

Magnetic susceptibility data of the $\text{HgBa}_2\text{CuO}_{4+x}$ are shown in Figure 2, which were obtained by using a SQUID magnetometer (Quantum Design) with an applied field $H_0=20$ G. The data clearly demonstrate a normal to superconducting transition with a T_c of about 92 K. If we assume an average density is about 6 g/cm³, the shield volume fraction (ZFC) amounts to about 70% and the flux expulsion fraction (FC)

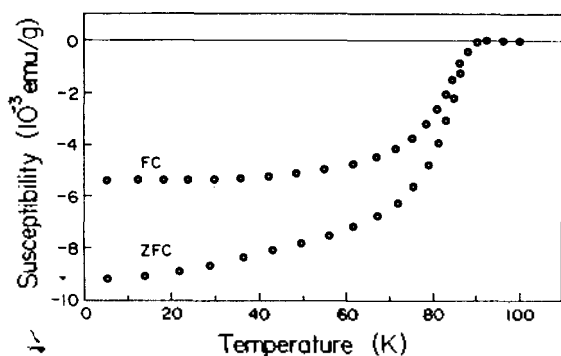


Figure 2. Magnetic susceptibility versus temperature for $\text{HgBa}_2\text{CuO}_{4+x}$ material with an applied magnetic field of 20 G.

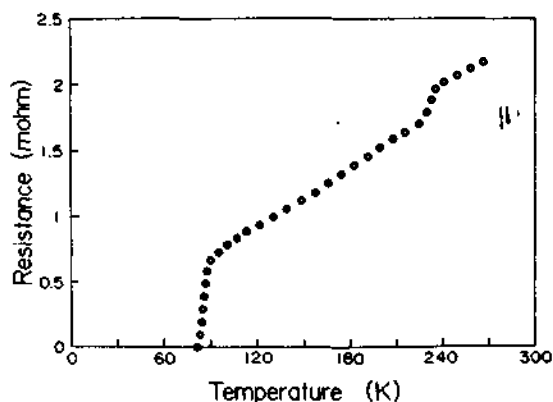


Figure 3. Resistance versus temperature for $\text{HgBa}_2\text{CuO}_{4+x}$ compound.

reaches about 42%. The resistance versus temperature for the same $\text{HgBa}_2\text{CuO}_{4+x}$ compound which was measured with use of a standard four probe method is shown in Figure 3. This displays a superconducting transition at 92 K and reaches zero at 84 K, which is agree well with the magnetic susceptibility data.

In summary, we have synthesized superconducting $\text{HgBa}_2\text{CuO}_{4+x}$ compound with use of $\text{Ba}_2\text{CuO}_{3+x}$ precursor. Isolation of pure $\text{HgBa}_2\text{CuO}_{4+x}$ samples largely depends on precursor materials and synthetic conditions, especially on moisture in air. We found that the $\text{HgBa}_2\text{CuO}_{4+x}$ has a tetragonal P4/*mmm* symmetry with lattice parameters $a=3.8868$ (2) Å and $c=9.4886$ (1) Å, and shows a bulk T_c of about 92 K. Currently, we are attempting to isolate structurally homologous series of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ ($n=2$ and 3) compounds.

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A Synthetic Approach to 2-Piperidylglycine (II)¹

Kyoo-hyun Chung*, Yi Yeoul Lou, and Won-seok Kim

Department of Chemistry, Inha University,
Inchon 402-751

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Heterocyclic derivatives of amino acids show some interesting pharmacologic properties. 2-Piperidylglycine (1) will be a model compound for the synthesis of streptolitin (2) and antitumor agent 593A (3).² Diastereoisomeric 2-piperidylglycine has been synthesized by extending Lowe's method for preparing nuclear analogues of penicillins,³ and by alkylation of glycine equivalent to C-2 position of piperidine ring.¹

We now report a straight forward synthesis of both diastereoisomers of α -amino-2-piperidineacetonitrile 8. Protected 2-piperidinecarbaldehydes (5) were obtained by the protections of 2-piperidinemethanol (4a) with benzyl (Bn), benzyl-oxy-carbonyl (Cbz) and t-butoxycarbonyl (t-Boc) group followed by Swern oxidation.⁵ Treatment of 2-piperidinecarbaldehyde 5 with KCN⁶ afforded α -hydroxy-2-piperidineacetonitrile 6.⁷

The α -hydroxy-2-piperidineacetonitrile 6 was reacted with ammonia in methanol to give α -amino-2-piperidineacetonitrile 8.

In Cbz case, the formation of bicyclic carbamate 7 was observed in THF-H₂O, and suppressed in the presence of ammonium chloride. The ratio of threo to erythro was about

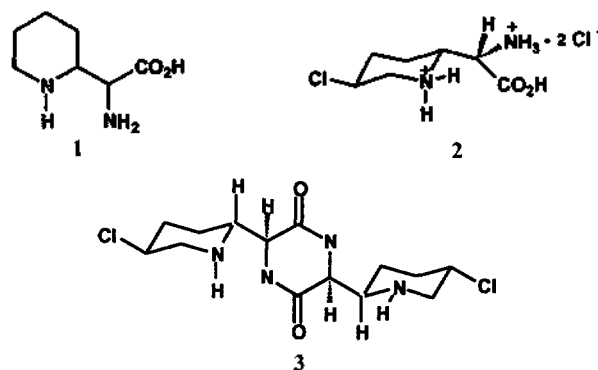


Figure 1.