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Rapid crystal growth of triple-layered cuprate superconductor HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ by cesium chloride additional method

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Abstract
We have developed the rapid growth method for HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (Hg-1223) by using a sealed quartz tube technique with a small amount of cesium chloride (CsCl). Our results suggested that a small amount of CsCl works as a flux during the crystal growth of Hg-1223. The developed method achieved the growth of the Hg-1223 single crystal pieces in 4 h. Furthermore, the grown single crystals showed high purity. The developed method is useful for application purposes such as high transition-temperature ($T_c$) superconducting cable.

1. Introduction

Mercury-based cuprate superconductor of HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2(n+1)+\delta}$ (Hg-122$n-1$), $n = 1, 2, 3, \ldots$, where $n$ is the number of CuO$_2$ planes in a unit cell. Especially Hg-1223, exhibits the highest superconducting transition temperature ($T_c$) of ∼138 K [1] among superconductors under ambient pressure. Such high $T_c$ makes Hg-1223 attractive for fundamental studies and also for technical applications. The synthesis of Hg-1223 is extremely difficult than other cuprate superconductors due to the toxicity and high volatility of mercury. It is required to synthesize them in a closed system such as under high pressure or in a sealed tube. In a high-pressure method, there is an advantage to obtain Hg-1223 single phases but this method produces only a small amount of the samples and requires a large-scale apparatus [2–4]. On the other hand, a preparation procedure of a sealed tube method is simpler than a high-pressure synthesis, yet it is not easy to synthesize Hg-1223 single phases because synthesis parameters are complexly involved with each other. It has been reported that to grow high quality Hg-1223 crystals by a sealed tube method, a total time of 100 h or more is necessary for any of the previous works [5–10]. Especially, the growth method recently developed by Loret [9] and Wang [10] is expected to make it possible to obtain large single crystals of Hg-1223 and stimulate basic research. However, in order to use Hg-1223 for large devices such as superconducting cable prepared by the powder-in-tube method, it is necessary to prepare large amount of high-purity Hg-1223 crystals rapidly.

To overcome the problems mentioned above, here we report the rapid crystal growth of Re-doped Hg-1223 single crystal by using the sealed quartz tube method with a small amount of CsCl which was expected to work as flux and often used for single crystals growth in a sealed quartz tube for, e.g., iron-based superconductor of SmOFeAs [11], bismuth chalcogenide-based superconductors of RE(O, F)Bi$_2$ (RE = La, Ce, Pr, Nd; Ch = S, Se) [12–14], and so on. Note that an amount ratio of flux and a material in this study is different from that of a conventional flux method: not a little material into much flux but a little flux into much material. By this idea, our developed method might be produce Hg-1223 single phases in larger quantities with rapidly than conventional sealed tube methods.
2. Method

The growth of Hg-1223 single crystals was based on a sealed quartz ampoule technique. The schematic drawing of the sample preparation is given in figure 1. First, the precursor powders having the cation ratios of Re:Ba:Ca:Cu = 0.2:2:2:3 were synthesized by a solid-state reaction method. Starting materials of high purity (more than 99.9%) ReO₂, BaCO₃, CaCO₃, and CuO were mixed in the above-mentioned ratios and heated at 900 °C for 12 h in air. The calcined powders were again reground and then calcinated at 900 °C for 12 h in air. The calcined precursor (~0.3 g) was mixed with HgO (~0.3 g) pelletized and put into an evacuated quartz ampoule. And then, a pellet of CoO (~0.28 g) as an oxygen getter was placed into the same ampoule to promote the growth of Hg-based superconducting phases (figure 1(a)). This ampoule with precursor was heated at 800 °C for 12 h. The obtained material was ground and mixed (this is first sintered powder in figure 1(b)) with HgO (~0.3 g) again with or without a small amount of CsCl (~0.03 g). The mixture was charged into an Al₂O₃ crucible, which was inserted into an evacuated quartz ampoule. A pellet of CoO (~0.28 g) was also placed into the same ampoule (as shown in figure 1(b)). This ampoule was heated at 840 °C for 4 h or 60 h followed by furnace cooling. Powder x-ray diffraction (XRD) pattern was measured by the θ–2θ method with CuKα₁ radiation using Mini Flex 600 (Rigaku). The sample morphology and the chemical composition were identified by a scanning electron microscope (SEM) using JSM6010-LA (JEOL) equipped with an energy dispersive x-ray analyzer (EDX) at the accelerated voltages of 5 kV and 20 kV. The magnetic susceptibility was measured under an applied field of 10 Oe using a magnetic property measurement system (MPMS; Quantum Design) with a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Figure 2 shows the powder XRD patterns of Hg-1223 grown at 840 °C with CsCl for 4 h and without CsCl for 4 h and 60 h. Powder XRD was measured by collecting and crushing small crystal pieces. The almost single phase of Hg-1223 formed in the 4 h synthesis with CsCl. The peak of CsCl (2θ ∼ 30.7°) was also found in the XRD pattern because CsCl was not removed from the sample. In the growth without CsCl, on the other hand, a long heating time of 60 h needed to obtain the almost single phase of Hg-1223. The short heating time of 4 h mainly produced the unreacted precursor phases of BaCuO₂ and Hg-1212. Thus, CsCl promotes the growth of Hg-1223 phase although the promotion mechanism is unclear at this time.

Figure 3(a) shows the SEM images of the synthesized sample without CsCl (840 °C for 60 h). This result shows that single crystal pieces just by sintering at 840 °C for 60 h. Figure 3(b) shows the SEM images of Hg-1223 crystals grown with CsCl (840 °C for 4 h). The grown crystals displayed plate-like crystalline samples with 5–20 μm in width and 1–3 μm in thickness and a small amounts of impurity grains. These pieces had a uniform surface, which is one of the characteristics of single crystals. In EDX analysis of the obtained crystals, only uniform surfaces of some cristal pieces were spot analyzed. Figure 3(c) shows the EDX analysis spectrum in Hg-1223 crystals grown with CsCl (840 °C for 4 h). As a result of EDX analysis, the chemical compositions normalized by the Cu element were estimated to be Hg₆₀.₉₇Re₀.₂₂Ba₂₀Ca₉Cu₃.₇O₈.₇₂, which was in good agreement with the ideal compositions of Hg₆₀.₉₇Re₀.₂₂Ba₂₀Ca₉Cu₃.₇O₈.₇₂. Moreover, the elements of Cs and Cl were not detected in the EDX spectra of each crystal and were found in that of the only impurity grains. The single crystals of Hg-1223 were grown independently, hence, indicating that CsCl worked as a flux intrinsically.

Figure 4 shows the temperature dependence of magnetic susceptibilities for the as-grown Hg-1223 crystals grown with CsCl. Magnetic susceptibility was measured by collecting as-grown crystal pieces without crushing. The data exhibit a sharp superconducting transition at 133 K for Hg-1223. The post-annealing for the obtained Hg-1223 at 250 °C–350 °C overnight under the oxygen atmosphere did not change the Tc, suggesting that the
oxygen deficiencies in (Hg/Re)O$_2$ plane did not exist in them due to the high Re-doping. The Hg-1223 exhibits the nearly highest $T_c$ compared to the previous data, which indicates that each phase is in a nearly optimal doped state.

From the results above, high-purity Hg-1223 crystals were grown in a short time by using the method of adding CsCl. The total time of the process according to our method is less than 60 h, which is shorter than any of the previous reports [5–10]. The future challenge is to achieve a sharp superconducting resistive transition by using rapidly grown Hg-1223 crystals. One of the solutions to overcome this problem will be increasing the size of the sample. In addition, the possibility of single crystal growth of Hg-1223 in a shorter than 4 h and the best ratio of CsCl are un-known problems, these issues should be clarified in the future study.

**Figure 2.** Powder XRD patterns of Hg-1223 grown at 840 °C with CsCl for 4 h and without (w/o) CsCl for 4 h and 60 h. The Miller index of Hg-1223 has been assigned. The triangles, the squares, and the dots show the peaks of HgBa$_2$Ca$_2$Cu$_2$O$_y$, BaCuO$_2$, and CsCl, respectively.

**Figure 3.** (a) SEM image of obtained crystals without CsCl (840 °C for 60 h), and (b) that of Hg-1223 crystals grown with CsCl (840 °C for 4 h). (c) EDX analysis spectrum in Hg-1223 crystals grown with CsCl (840 °C for 4 h).
4. Conclusions

In conclusion, we have successfully developed the rapid growth method for Re-doped Hg-1223 in 4 h at the earliest. It has been achieved by using the sealed quartz tube method with a bit of CsCl flux. The XRD measurement revealed that CsCl can promote the growth of Hg-1223 phases. Our developed rapid growth method is useful to fabricate Hg-based superconducting cable using, e.g., a powder-in-tube method.

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