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Short Communication

Superconducting Cuprates and Related Oxides XI. Aluminium Contamination of Flux-Grown Crystals of $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$

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The top seeded preparation of $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ crystals from a BaO–CuO flux in Al_2O_3 crucibles has been reported recently.[1] The problem with this growth mode is that the flux corrodes the crucible and Al is found in the cuprate crystals. Microprobe analyses have shown that the Al content is significant, and the compositions $YBa_2Cu_{2.87(8)}Al_{0.10(1)}O_{6.31(2)}$[2] and $PrBa_2Cu_{2.75(3)}Al_{0.10(1)}O_{6.64(10)}$[1] have been reported. The aluminium atoms are substituting the Cu1 atoms in the structure, which have an effect on the superconducting properties. Different attempts have been made to reduce or even eliminate the Al content in the cuprate single crystals. A possibility is to add compounds like B_2O_3, Bi_2O_3 and or BaF_2 to the flux, which has been reported to reduce the Al content in the cuprate single crystals.[3–6] Another approach is to reduce the contact between the flux and the Al_2O_3 crucible by a protecting layer on the inside of the crucible or by using an aluminium free crucible inside the Al_2O_3 crucible. This has been tested in the present investigation.

Experimental and results

The chemicals used in the growth experiments were: Y_2O_3, 99.99%, and Pr_6O_{11}, 99.9%, from Auer-Remy, BaO, 97.5%, Johnson Matthey, BaO_2, 95%, Aldrich, and CuO, p.a., Merck. The crucibles used were made of Al_2O_3, Y_2O_3, ZrO_2 and $BaZrO_3$. The growth experiments were performed using a double crucible arrangement sketched in Fig. 1. Crucible 1 was typically a commercially available crucible of Al_2O_3 or ZrO_2. Crucible 2 was either a commercially available crucible or was a layer made of Y_2BaCuO_5 or of $BaPrO_3$ which were made from stoichiometric mixtures of Y_2O_3, BaO, CuO,[7] or of Pr_6O_{11}, BaO,[8] respectively, and reacted at 900 °C for 12 h. The wall thickness of the layers was approximately 10 mm, with a density of 50% of the theoretical density. The BaO–CuO mixture was reacted in a ZrO_2 crucible and had the nominal composition $Ba_3Cu_7O_{10}$. The flux composition in the growth experiments was typically 15 mol% $Y(Pr)Ba_2Cu_3O_7$ and 85 mol% $Ba_3Cu_7O_{10}$.

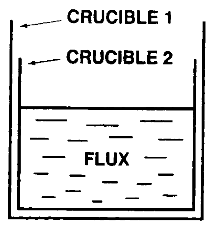

Fig. 1. Sketch of a double crucible arrangement used in the flux growth of cuprates.

The crystal growth furnace used was of the type described previously and the temperature–time profile of the experiment was also as described previously.[1] The charge was melted at the temperature T_m, and the sample was then slowly cooled to the temperature T_l. During cooling the temperature of the melt surface was higher than that of the bottom of the crucible. The accelerated crucible rotation technique was used to prevent precipitation of crystals on the surface of the melt. Then the thermal gradient over the crucible was reversed, and a single crystal seed was introduced to the surface of the melt at the temperature T_c. Growth of the crystal on the

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seed took typically 10–14 days to obtain a crystal of the dimensions $7 \times 7 \times 3$ mm^3. Microprobe analyses were made of the grown crystals as described previously.[1] Typical results of the growth experiments are reported below

$YBa_2Cu_3O_7$ crystal. $T_m = 1000$ °C, $T_l = 950$ °C, $T_c = 963$ °C. Crucible of Al_2O_3 with inside layer of Y_2BaCuO_5: The inside layer was the yttrium source but was, however, not sufficiently dense to prevent contamination of the melt with aluminium. Microprobe analysis of the grown crystal gave the composition $Y_{0.97(5)}Ba_{2.02(3)}Cu_{2.77(5)}Al_{0.11(5)}O_{6.41(5)}$. The aluminium content is thus comparable with that of a crystal grown from an Al_2O_3 crucible, the composition of which was $YBa_2Cu_{2.87}Al_{0.10}O_{6.31}$.[2]

Crucible of ZrO_2 with inside layer of Y_2BaCuO_5: After 1–2 days the seed crystal of $YBa_2Cu_3O_{7-\delta}$ began to dissolve and the Y_2BaCuO_5 phase started to precipitate on the seed crystal. The ZrO_2 crucible was strongly corroded by the flux.

Crucible of Al_2O_3 with an inside crucible of Y_2O_3: The melt penetrated through the Y_2O_3 crucible wall 10–20 h after the flux had been melted. However, the growth experiment could continue.

$PrBa_2Cu_3O_7$ crystal. $T_m = 980$ °C, $T_l = 930$ °C, $T_c = 943$ °C. Crucible of Al_2O_3 with an inside layer of $BaPrO_3$: A 10 l h^{-1} gas flow of Ar was used to reduce the oxygen content in the furnace. The microprobe composition of the grown crystal was $Pr_{1.03(4)}Ba_{2.00(5)}Cu_{2.75(5)}Al_{0.19(2)}O_{6.58(6)}$. The growth experiment gave thus a crystal with a considerable content of aluminium.

Crucible of $BaZrO_3$ inside a crucible of Al_2O_3: For this growth experiment we used a BaO which contained SrO. The microprobe analysis gave the composition $Pr_{1.04(2)}Ba_{2.01(2)}Sr_{0.04(2)}Cu_{2.73(2)}Al_{0.06(2)}O_{6.40(2)}$. The aluminium content of the crystal is still significant but is, however, reduced compared to the composition of the crystal $PrBa_2Cu_{2.75}Al_{0.10}O_{6.64}$ grown from a crucible of Al_2O_3.[1]

Crucible of Y_2O_3 inside a crucible of ZrO_2: A seed crystal of $YBa_2Cu_{2.8}Al_{0.1}O_{7-\delta}$ was used mounted on a holder of MgO fixed on a rod of Al_2O_3. The flux contained praseodymium oxide and the Y_2O_3 crucible was the yttrium source for the growth of a $(Y,Pr)Ba_2Cu_3O_{7-\delta}$ crystal. An argon gas flow of 10 l h^{-1} was used and the crystal growth took 17 days. The composition of the crystal was according to microprobe analysis $Y_{0.13(6)}Pr_{0.92(4)}Ba_{1.93(8)}Cu_{2.83(9)}Al_{0.04(1)}O_{6.45(7)}$. This crystal had the lowest aluminium content of the grown crystals. In this experiment the aluminium source was only the seed crystal and the Al_2O_3 rod on which the seed crystal and the MgO seed holder was mounted.

Conclusion

The top seeded preparation of $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ crystals from a BaO–CuO flux kept in a crucible requires a small vertical temperature gradient in the crucible to transport material from the feed to the growing crystal and a growth time of 1–3 weeks to obtain large crystals. Commercially available crucibles of Al_2O_3 were mechanically stable for the growth experiments but corroded. Inside layers of Y_2O_3, Y_2BaCuO_5 or $PrBaO_3$, which are also the yttrium or praseodymium sources for the crystals, only reduce the aluminium content of the grown crystals compared to crystals grown in Al_2O_3 crucibles without any of the abovementioned layers when these layers are dense. However, the layers used in the present investigation have not been sufficiently dense to prevent the flux from penetrating the layers and corrode the Al_2O_3 crucibles. The crystals obtained in this project had volumes up to 0.5 cm^3 and will be used to investigate physical properties of high-T_c superconductors by elastic and inelastic neutron scattering.

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