

SINGLE CRYSTAL PREPARATION OF CuO

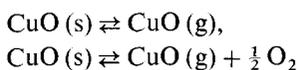
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Single crystals of CuO are prepared by means of sublimation in a closed quartz capsule at 900 °C. The crystals have dimensions of 5 × 2 × 0.2 mm. Doping of the CuO with a few percent In₂O₃ (1 to 5% In/(In+Cu)) was necessary for the growth of the crystals. The residue contained CuO–In₂O₃ spinel.

In the literature on CuO no attempts have been reported to our knowledge to prepare CuO crystals by sublimation. A study of the behaviour of CuO between 600 °C and 900 °C has been made by several authors^{1–7}). Brewer and Mastick⁶) thought that the stability of gaseous copper (II) oxide is proved by the measurement of the vapor pressure of solid oxide by Mack, Osterhof and Krauer⁷). They considered the following equilibria:



The vapor pressures of solid copper (II) oxide between 873 and 1223 °K were higher by factors of 10⁶–10⁸ than those of gaseous copper which is in equilibrium with solid copper (II) oxide as calculated from the heat of formation of CuO(s). Kodera et al.¹) used a mass spectrometer to analyse the gases evaporated from CuO at constant temperature. Only O₂, H₂O, CO and CO₂ were detected; the residue of Cu₂O. They concluded therefore that CuO does not vaporize, but this result is probably due to the experimental procedure used by the authors.

For the preparation of the mixture CuO–In₂O₃ we used CuO from Baker (Baker Analyzed Reagent) and In₂O₃ from BDH (Laboratory Reagent). The mixtures contained 1%, 2% and 5 at% In/(In+Cu).

The component oxides were mixed by handgrinding in an agate mortar, and the mixture was pelleted at a pressure of 1000 kg/cm². The pellets were 8 mm in dia-

meter and 2 to 3 mm thickness. The quartz tube with a diameter of 15 mm was first cleaned with a solution of perchromic acid and afterwards successively rinsed with distilled water and acetone. The pellets were placed in the tube on a platinum gauze or in an Al₂O₃ boat, and then the tube was sealed off. The quartz capsule was placed horizontally in an electric furnace. The furnace temperature was 900 °C, and between the upper and lower wall of the capsule a temperature difference of about 10 °C existed. The time the capsule was held in the furnace ranged from 2 days to one week. The free volume of the capsule was about 14 cm³, and the amount of oxide in the form of pellets sealed in the capsule ranged from 0.6 to 0.8 g.

About 100 to 300 mg CuO crystals were grown on the upper wall depending on the time the capsule was held in the furnace. The pO₂ variation had almost no influence. The crystals obtained in this way were black. They had dimensions from 1 × 0.5 × 0.1 mm to 5 × 2 × 0.2 mm. Powder X-ray diffraction revealed that the crystals were CuO and neither In₂O₃ nor a CuO–In₂O₃ compound could be detected. Determination of In in the crystals by flame spectrometry gave no results (< 0.05 wt% In), with neutron activation analysis 0.02 wt% In was detected. On the remainder of the CuO–In₂O₃ pellet a green powder was present and of some the solid part consisted of a layer with a greenish outlook and there upon a layer of micro-crystalline black CuO.

If the capsule had been in the furnace for a week,

only a green powder was left. The analysis of one of these powders gave 4.2 CuO–In₂O₃, probably a mixture of 5 CuO · In₂O₃ with 2.3 CuO · In₂O₃⁸). The wall of the quartz capsule was partially covered with white/blue crystals. The blue crystals were probably CuSiO₃ and the white crystals were probably cristobalite. If the furnace temperature was below 850 °C, no crystals were grown on the upper wall. Experiments with CuO without In₂O₃ yielded negative results. (Only a very faint black cloud could be seen on the upper wall after one week.) There was no difference in the behaviour when an Al₂O₃ boat was used instead of Pt gauze.

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