

Crystals of Hg superconductors

SIR — Solid-state high-pressure techniques are very useful for synthesizing polycrystalline copper oxide superconductors, including the recently discovered $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ (Hg-12($n-1$) n) and the infinite-layer compound $\text{Ca}_{1-x}\text{A}_x\text{CuO}_2$ (where A is an alkaline earth metal)^{1,2}. High pressure, produced

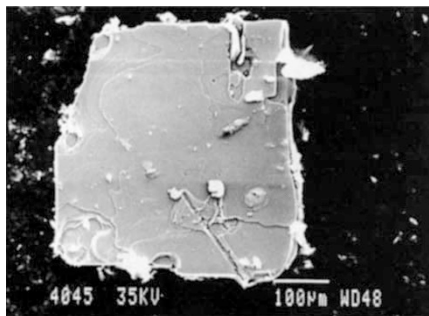


FIG 1. $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ single crystal with characteristic growth steps on the surface (P. Wägli).

by a solid medium such as pyrophyllite, prevents mercury evaporation in the former and stabilizes the structure in the latter. But the sample mass is limited up to several hundred milligrams, there is no free space to grow single crystals, the pressure and temperature distribution are not homogeneous and the partial oxygen pressure cannot be controlled. We have developed a gas-phase high-pressure technique which circumvents these problems and which has allowed us to grow single crystals of Hg-12($n-1$) n of millimetre size.

The main advantages of this method compared with the solid-state pressure medium technique are: (1) the use of an Ar gas atmosphere with a defined partial oxygen pressure leaves free space for the single crystal growth; (2) pressurized Ar gas acts as an encapsulation of the sample, preventing evaporation of Hg; (3) the temperature gradient can be controlled in a three-zone furnace; and (4) the sample volume can be as large as several cm^3 .

The experimental high pressure system consists of a "Unipress" gas compressor 15-kbar and a piston-cylinder pressure chamber with an internal three zone Kanthal furnace^{3,4}.

The Hg-12($n-1$) n compounds melt peritectically, but at ambient pressure decompose before melting and the volatile components evaporate. Because of the high density of Ar gas at this pressure the evaporation of Hg is strongly suppressed. Application of a flux with a lower melting point allows growth of single crystals below the peritectic decomposition temperature. Mixtures of the stoichiometric Hg-1223 with 10 atom % PbO or 50 atom % BaCuO_2 plus CuO have been

used as a flux in several crystal-growth experiments. Parameters of the crystal growth process were: $p_{\text{Ar}} = 10$ kbar, $T_{\text{max}} = 1,040 - 1,070$ °C, a cooling rate of 5–20 °C per hour down to 1,020 °C followed by a cooling rate of 10 °C per min to 20 °C.

As a result, single crystals of the Hg-12($n-1$) n compounds (with $n = 3, 4$ and 5) have been obtained. For the Hg-1234 single crystals a T_c of 129 K was observed, which is higher than 126 K reported previously (J. Capponi, unpublished data). In Fig. 1, the Hg-1234 single crystal is shown with characteristic growth steps on the surface. A separation of the crystals from the flux is very difficult, so we have obtained pieces only of size up to $0.5 \times 0.5 \text{ mm}^2$. We expect to optimize the crystal growth process to obtain larger crystals.

A Hg-1234 crystal was measured on an X-ray four-circle single-crystal diffractometer, using $\text{MoK}\alpha$ radiation ($\lambda = 0.7103$ Å). The space group is $P4/mmm$ and the lattice parameters are $a = b = 3.8478$ Å, $c = 18.982$ Å (Fig. 2). The assumed four-layer structure was confirmed, the refinements converged at $R = 0.064$. In the c -direction, the structure contains four CuO_2 layers separated by Ca atoms. They are sandwiched by two Ba–O layers which include one Hg–Pb–O plane.

The application of the gas high pressure technique to Hg-12($n-1$) n family will allow optimization of the synthesis and crystal growth in thermodynamically well defined conditions.

During the preparation of this manuscript, a paper concerning structural investigations of Hg-1212 and Hg-1223 single crystals of a maximum size 30 μm obtained by recrystallization of a powder has been published⁵. More details concerning our high pressure growth method and the structure and properties of Hg-12($n-1$) n and CaCuO_2 infinite layer

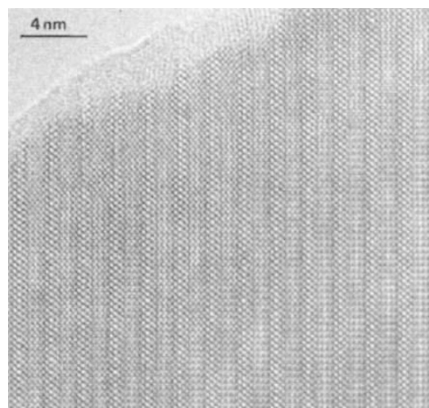


FIG 2. High-resolution transmission electron micrograph of a perfect structure of the Hg-1234 single crystal (R. Wessiken and H.-U. Nissen). Scale bar, 4nm.

superconducting single crystals will be presented elsewhere⁶.

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Plant survival

SIR — Grabherr *et al.* in their Scientific Correspondence¹ present a grim prognosis for montane plants trying to keep up with global warming. But the situation could be even worse. Climate change will probably involve both temperature and precipitation changes at most locations². When two physical factors change, the range of a species may not only shift, but may also change in size because the upper and lower limits of a species are not determined by the same factor³. For example, the range of intertidal barnacles is limited by desiccation from above and interspecific competition from below⁴. For plants along gradients of latitude or elevation, temperature often determines the upper limit^{5–7}, whereas moisture⁵ or carbon balance⁸ (at least partly dependent on moisture availability) often determine the lower limit. Wherever temperature increases and moisture decreases (a frequent occurrence in many models²), the range of a species is likely to shrink as well as shift. Therefore, predictions about the effect of climate change on plant distributions need to take both temperature and moisture into account.

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