Crystal growth under high pressure: preparation of the spin-ladder compound SrCu$_2$O$_3$

Crystal growth under high pressure: preparation of the spin-ladder compound $SrCu_2O_3$

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Abstract
The two-leg ladder $SrCu_2O_3$ belongs to the homologous series $Sr_{n-1}Cu_nO_{2n-1}$ and was first synthesized by Hiroi *et al* (Hiroi Z, Azuma M, Takano M and Bando Y 1991 *J. Solid State Chem.* **95** 230). Due to the massive reaction of the sample material with the crucible (Au or Pt), only short reaction times up to 30 min have been used typically. We suggest an improved composite crucible with a single-crystalline MgO inset in a sealed Pt capsule and demonstrate its capability for single-crystal growth of $SrCu_2O_3$. Experiments with a typical duration of 15 h were conducted at pressures between 3 and 6 GPa at temperatures between 950 and 1500 °C. Slow cooling of the melt effected directed growth of the first $SrCu_2O_3$ milimetre-sized single crystals.

1. Introduction

High-pressure synthesis at several gigapascals was successfully used to prepare new compounds with a close structural relationship to high-Tc superconductors, which could not be synthesized otherwise, i.e. at ambient pressure. Special attention has been paid to the so-called 'spin-ladder' compounds, which may be seen as an intermediate case between magnetically one- and two-dimensional compounds from a structural viewpoint [1].

In the case of $SrCu_2O_3$, the spin ladders consist of corner-sharing CuO_4 plaquettes, arranged in CuO_2 sheets, which are stacked along the c-axis and separated by strontium atoms. Synthesis of $SrCu_2O_3$ (which belongs to the homologous series $Sr_{n-1}Cu_{n+1}O_{2n}$ with $n = 3$) was first described by Hiroi *et al* [2]. Using a high-pressure treatment (6 GPa, 1000–1300 °C, 0.5 h) a polycrystalline material could be synthesized, which was sufficient for structure determination by powder x-ray diffraction (XRD), electron diffraction and high-resolution electron microscopy (HREM). After this, some other groups succeeded in preparing polycrystalline material by solid-state reaction under comparable conditions [3–6], but no single crystals could be grown so far, since the precursor strongly reacts with conventional crucible materials such as gold or platinum. In principle, melt or flux growth should yield crystals of higher quality compared to a solid-state reaction, but does not seem to be applicable in this case, since crucible corrosion severely limits the useful growth time.
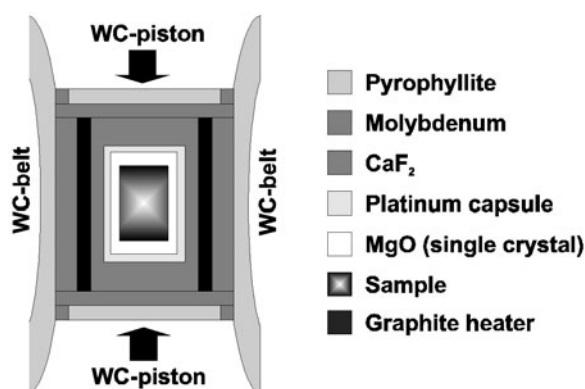
Figure 1. A schematic diagram of the sample assembly built in the belt press.

In this work, we evaluate various crucible materials with respect to their suitability for crystal growth of $SrCu_2O_3$ and present first results with a new kind of compound crucible.

2. Experimental details

The precursor for high-pressure synthesis of $SrCu_2O_3$ was prepared by mixing the ambient-pressure phases $SrCuO_2$ and CuO in appropriate ratios. $SrCuO_2$ was prepared by solid-state reaction of $SrCO_3$ and CuO (each 99.99%). The mixture was ground in an agate mill and calcined in air at 1030 °C for 12 h. This procedure was repeated three times to ensure a homogeneous product; phase purity was monitored by powder XRD after each step.

For all high-pressure experiments described here, the precursor has been sealed in metallic capsules with an inner diameter of 4 mm (rather than wrappings of metal foil as sometimes described in the literature) to keep the oxygen content in the sample as constant as possible during high-pressure and high-temperature treatment. Sealing has been done by arc welding under protective atmosphere. Since crucible corrosion is an important issue here, results on this topic are discussed in more detail in the next section.

For pressure generation a belt press was used. A torus-like tungsten carbide core encloses the sample assembly with the pressure transmitting media CaF_2 and pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) as shown in figure 1. Two pistons working against each other and onto the sample assembly are driven by a 4900 kN hydraulic ram. The pistons conduct an electrical current of about 200 A, which is transferred through the assembly via a graphite tube used as a resistance heater. The pressure is controlled and calibrated by the oil pressure. Temperature is measured by a thermocouple which is placed directly below the crucible. With this set-up, a good spatial and temporal temperature homogeneity (± 7 K) and pressure accuracy ($\pm 1\%$) could be achieved in the sample volume [7].

Phase analysis of the grown samples is performed by a Siemens D500 x-ray diffractometer. The microscopic composition is measured by Zeiss DSM 940 A scanning electron microscope with a Microspec WDX-2 A unit for wavelength dispersive x-ray analysis (WDX). Crystals of different orientation were identified by optical polarization microscopy.

3. Crucible reactions

Desirable properties of an ideal crucible for melt growth of $SrCu_2O_3$ under high pressure are easily described:
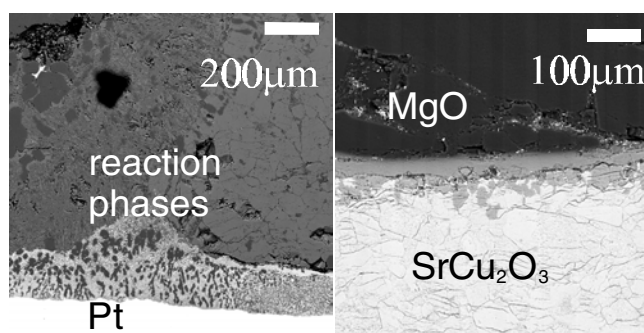
Figure 2. SEM graphics of the sample: with a Pt crucible after 10 min of processing time at 6 GPa at 1300 °C (left); with an MgO inner crucible after 5 h at 4 GPa and 1300 °C (right).

(1) to keep the oxygen in the sample volume during growth, the crucible should be gas-tight,
(2) the crucible material should not react with SrO–CuO melts,
(3) the melting point should be well above the intended operation temperature and
(4) the material should be machinable with reasonable effort.

It is quite clear that not all these properties will be found in one material, but a compromise has to be found experimentally.

The intended operation temperature is not exactly known in the case of SrCu$_2$O$_3$ since a complete phase diagram has not been published so far. Kobayashi *et al* [4] observed partial melting at 1050 °C of a sample containing 75 mol% CuO, but no melting was observed at 3 GPa up to 1150 °C for a sample with 66.6 mol% CuO (equivalent to SrCu$_2$O$_3$). If SrCu$_2$O$_3$ melts congruently, growth from a stoichiometric melt would be preferable but requires a crucible stable at temperatures higher than 1150 °C. Otherwise, a non-stoichiometric melt has to be used anyway, and a lower temperature might be sufficient.

In view of this, gold capsules (although typically used in the literature [2–4]), are not ideal, since the melting point of gold (1064 °C at ambient pressure, rising to 1404 °C at 6.5 GPa [8]) is close to the temperature range mentioned above. Reactions of gold with the sample material, as reported in the literature [9], may further decrease the maximum usable temperature.

The use of platinum seems to be attractive because of its higher melting point (1772 °C at ambient pressure), but experiments show that platinum is corroded severely by SrO–CuO melts. As shown in figure 2 at 1300 °C and 6 GPa a reaction layer of (Sr, Cu)$_4$PtO$_6$ and other phases quickly develops (about 0.5 mm thickness in 10 min). For short reaction times, platinum may be used, but only the remaining core material is free from unwanted reaction products. Also in a comparison by Wang *et al* [9], at 6 GPa platinum is suggested for use only up to 1050 °C, and even gold is considered to be better suited (recommended there up to 1150 °C).

Molybdenum has an even higher melting point (2617 °C), but due to its lower electronegativity compared to copper, molybdenum oxides are formed. Tantalum (with or without a protective layer of TaC) could not be used for the same reason: the formation of Ta$_2$O$_5$ and CuTa$_2$O$_6$ was observed.

At this point, no further experiments have been conducted with 'metal-only' crucibles, and several refractory materials have been tested for their compatibility with SrO–CuO melts. In order not to sacrifice the advantage of having a gas-tight capsule, these materials are planned for use as inset crucibles in a compound system, protecting an enclosing metallic capsule from corrosion. Alumina proved not to be useful, since it is easily penetrated by the melt due to
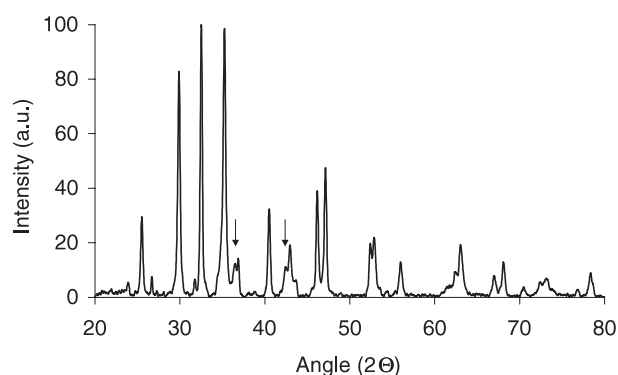
Figure 3. The x-ray powder pattern of SrCu$_2$O$_3$. A small content of Cu$_2$O is indicated by arrows.

its remaining porosity. Boron nitride (h-BN) is sometimes used in high-pressure experiments, because it is soft and easy to machine, but for contact with SrCuO$_2$ and CuO, borates like SrB$_2$O$_4$ appear.

Krauns *et al* [10] investigated wetting properties of some ceramic and single-crystalline materials in Ba–Cu–O melts, which are likely to behave comparably to SrO–CuO melts. Single-crystalline MgO (sc-MgO) was observed to have the lowest wetting tendency and best long-time stability. For polycrystalline (ceramic) MgO, slow dissolving was observed but this is expected to be further reduced with sc-MgO. Since sc-MgO easily cleaves parallel to $\langle 100 \rangle$ planes and thus cannot transfer shear forces, 'pressure shielding' is not an issue here.

Experiments with sc-MgO inset crucibles in platinum capsules reveal strongly reduced corrosion which makes this material superior to all other materials tested (see figure 2). Only a thin corrosion layer consisting of MgCu$_2$O$_3$ and other phases could be observed, with a thickness depending on temperature and duration. Experiments at 1500 °C at 5 GPa with a duration up to 15 h were rendered possible. A small amount of magnesium (lower than 3 at.%) is dissolved into the melt and built into the crystals. But it is expected that it will not be the ladders that are contaminated with Mg but the separating Sr layers which are not so important for the magnetic properties. At lower temperatures, growth might occur for a longer time. Therefore, the growth experiments described in the next section have all been performed with this kind of compound crucible.

4. Crystal growth

To get an overview of the phase stability, and to test the previous published phase diagram up to 1150 °C [4], different pressures varying from 3 to 6 GPa were investigated. For all applied pressures SrCu$_2$O$_3$ could be synthesized as the dominating phase, with a small amount of Cu$_2$O as can be seen from XRD (see figure 3). With all other crucible materials discussed in the previous section, and processing times longer than 30 min, SrCu$_2$O$_3$ appears as a minority phase or not at all, because of strong reactions with the crucible.

The phase diagram above 1200 °C has not been described in the literature. If we are to use melt growth in place of solid-state reaction, it is important to know whether direct growth from a stoichiometric melt is possible or whether a peritectic reaction takes place. We focused our investigation on 5 GPa and used three different compositions for growth experiments. CuO contents of 66.6, 75 and 85 mol% were used, because on the CuO-deficient side of SrCu$_2$O$_3$ other phases such as Sr$_{14}$Cu$_{24}$O$_{41}$ and all members of the above-mentioned homologous series
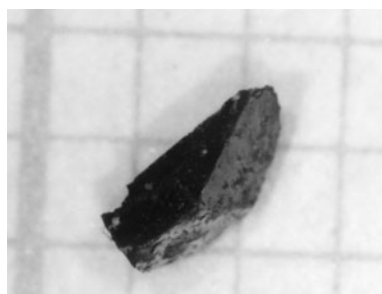
Figure 4. A photograph of a grown single crystal on a millimetre grid.

are stoichiometrically quite near to the targeted compound. Working on the CuO-rich side thus prevents complications due to formation of multiple phase mixtures. Heating up to 1500 °C, where the mixture is completely molten, and after a short homogenizing period, the temperature was lowered to 1350 °C at a rate of 10 °C h^{-1}.

It is concluded from micrographs and WDX analysis that on cooling a stoichiometric mixture a properitectic phase with lower CuO content compared to SrCu$_2$O$_3$ solidifies first. Subsequently, SrCu$_2$O$_3$ solidifies; it is not completely clear yet to what extent the properitectic phase is involved in this reaction; in other words, whether SrCu$_2$O$_3$ solidifies from the remaining melt only or a peritectic solidification occurs.

The maximum dimensions of the grown single crystals are 2 mm × 0.6 mm × 0.5 mm. Polarization microscopy shows that the samples are indeed single crystalline although a few inclusions and pores are present; see figure 4. The composition was verified by WDX to be SrCu$_2$O$_3$ and powder XRD yielded the correct structure. Unfortunately, no clear solidification front can be observed in the experiments with higher CuO content, which may help to clarify the phase diagram.

More experiments are needed before it can be clearly stated whether primary solidification from a non-stoichiometric melt is possible.

5. Conclusions

For melt growth of SrCu$_2$O$_3$ a gas-tight crucible with a low reactivity with the melt is essential. Single-crystalline MgO has been found to have the lowest reactivity and the best time stability. Single-crystal MgO with a sealed Pt capsule is a suitable composite crucible for melt growth of SrCu$_2$O$_3$ at high pressures. Crystal growth was performed using a belt press at 5 GPa and by lowering the temperature from 1500 to 1350 °C. Single crystals with maximum size of 2 mm × 0.6 mm could be grown, although the exact solidification path is not clear yet.

Acknowledgment

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