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STRUCTURAL AND THERMAL PROPERTIES OF THE HTSC Hg-1201

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Abstract

The lattice parameters of $Hg_xBa_2CuO_{4+\delta}$ were determined by X-ray powder diffraction as a function of temperature from 10 to 310 K. The fitting of the parameters yielded the thermal expansion coefficients of the superconducting oxide and demonstrated the anisotropy characteristics of the polycrystalline material. The effect of the irreversible loss of Hg on the lattice parameters is reported.

Keywords: $Hg_xBa_2CuO_{4+\delta}$, structural and thermal properties

Introduction

The discovery of superconductivity in the range 94–97 K in $HgBa_2CuO_{4+\delta}$ (Hg-1201) by Putilin *et al.* [1] generated a great deal of interest in this system. By means of X-ray diffraction, they were able to identify the excess of oxygen defects δ in the Hg plane and to estimate its amount as 0.10(3) atoms per formula unit.

Successively, Wagner *et al.* [2] synthesized $HgBa_2CuO_{4+\delta}$ and characterized its crystal structure and also the influence of oxygen on its superconducting properties. Their neutron powder diffraction data afforded evidence of a defect in the Hg plane, involving the substitution of copper for about 8% of Hg, and the occupancy of the Hg sites was observed to be approximately 3% deficient.

This deficiency was reported by almost all authors (see, for example, [3–5]), but was comparatively less well studied than the oxygen excess as it seemed not to degrade the superconducting critical temperature, T_c.

The stoichiometry of Hg in Hg-1201 depends on the preparation route, as it has been well demonstrated that O_2 is lost reversibly and Hg irreversibly [5].

Many synthesis routes have been reported in the literature. Samples with the nominal composition $HgBa_2CuO_{4+\delta}$ are generally prepared from stoichiometric mixtures of HgO and Ba_2CuO_3, but the synthesis may be performed at high pressure [6], in evacuated sealed silica tubes [1], in silica tubes and at static air pressure [7], in a temperature gradient so as to be able to control the vapour pressure of HgO [8], and so on.

Here, we report a novel method for the synthesis of superconducting samples of Hg-1201, at a constant total pressure of 1 atm, in which the stoichiometric index of Hg ranges from 0.5 to 0.8.

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Experimental

The compound $Hg_xBa_2CuO_{4+\delta}$ was prepared in the solid-state reaction between Ba_2CuO_3 and HgO (2N5). The single-phase precursor Ba_2CuO_3 was obtained by thermal decomposition of a stoichiometric mixture of BaO_2 (2N, Material Research), instead of $BaCO_3$ [9], and CuO (2N, Merck). Batches of about 30 g were prepared by the usual dry powder method, with thorough mixing of the starting oxides in a rotating mixer. The precursor powders were first reacted in air at about 1240 K for 40 min (heating rate: 50 K h^{-1}), heated at 1170 K for 6 h, and then slowly cooled to room temperature. The compound was weighed to determine the reaction mass loss, and then finely powdered, dry-sieved and structurally characterized to verify the single phase of the material.

The HgO and Ba_2CuO_3 powders were next mixed together in stoichiometric ratio and placed in an Al_2O_3 open crucible in a long silica tube emerging about 50 cm out of a vertical furnace, so that the sample stays at high temperature and mercury vapour is condensed just out of the furnace, on the wall of the silica tube, and can eventually drop down again into the furnace. The total pressure is maintained at 1 atm by a gas ballast system previously filled with pure O_2.

All samples were heated to 900 K for 6 h and then cooled to room temperature. This preparation method permits a very easy, quick and sure experimental procedure.

The dissociation reaction of the product oxide [4] is governed by an equilibrium constant K_D, depending on the partial pressures of oxygen and mercury; since K_D is likely to increase with increasing temperature, the mercury lost will be determined by the maximum temperature reached during the formation reaction.

At the end of the reaction, the mercury condensed on the wall of the silica tube is carefully collected and weighed. The sample is weighed too to check the consistency of the loss of mercury. Part of the sample, if it proved to be a single phase, was heated in oxygen to about 1250 K, to allow the complete loss of mercury for further verification.

At this stage, we observed differences in the mercury lost as a function of the maximum temperature reached during the formation reaction.

We repeated the experiments in an attempt to obtain a stoichiometric compound of Hg-1201, adding an excess of HgO equal to the loss to the starting mixture. At the end of process, performed under the same conditions, the amount of mercury in the sample remained the same, thereby proving the presence of a chemical equilibrium. Moreover, the lattice parameters were found to be the same within experimental error.

At 50% of stoichiometric mercury, the presence of secondary phases was found, followed by a complete disappearance of the superconductivity at 77 K.

The crystal structure of Hg-1201 was investigated by the X-ray powder method, using CuK_α radiation. The intensity calculations for the powder pattern were performed with least-squares Lazy Pulverix program [10].

Low-temperature measurements of lattice parameters were carried out with a Hüber low-temperature computer-controlled Guinier camera. The measurements were performed by adding silicon to the powders in order to provide a calibration

of the lattice parameters with an internal standard whose thermal expansion at low temperatures is well known [11]. An accuracy of better than $\Delta a/a = 10^{-4}$ can easily be obtained, but in this case the scattering of the data is relatively high due to the high absorption factor of the compound containing barium.

Resistivity tests were performed by the conventional four-wire technique with current reversal, in which the wires were silver-pasted onto the samples.

Results

Figure 1 reports the tetragonal P4/mmm (No. 123) structure type of stoichiometric Hg-1201. The octahedral coordination of the Cu in the CuO_2 planes with the apical oxygens (full circles) is not indicated. The excess oxygen defect is located in the Hg plane.

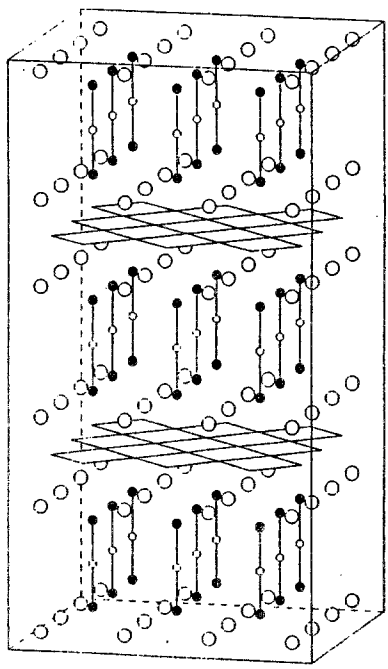

Fig. 1 Structure of stoichiometric Hg-1201. The planes are CuO_2, the small open circles (o) are mercury atoms, the small full circles (•) are oxygen atoms out of the planes and the large circles (O) are barium atoms

In can be observed that Hg (small open circles) is sandwiched in the middle of the CuO_2 planes. Thus, it is likely that, if Hg ion is lost without being replaced by another ion, an influence on the lattice parameters could be observed.

Wagner *et al.* [2] found that Cu could effectively replace Hg in its site, and the amount of the Hg vacancies is then less than 3% both in oxygenated and in reduced samples with annealing in argon at 500°C for 24 h. This is in contrast with the re-

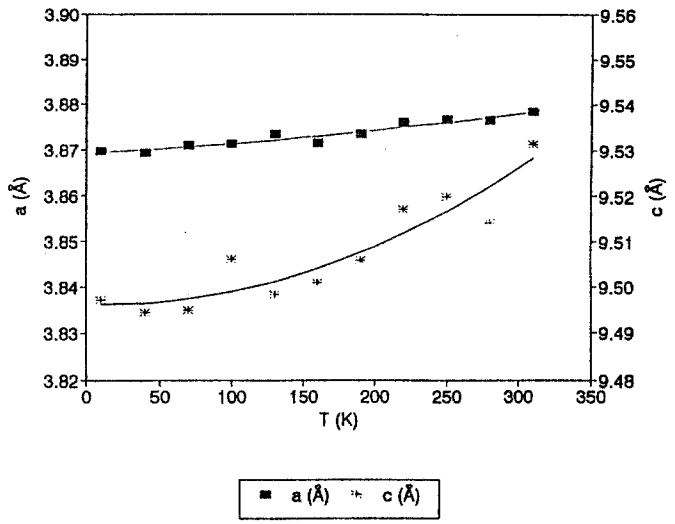

Fig. 2 Temperature dependence of Hg-1201 lattice parameters a (Å) (■) and c (Å) (*)

sults of Xiong *et al.* [5], who showed the decomposition of Hg-1201 under these conditions.

Figure 2 presents the dependence of the lattice parameters on temperature from 10 to 310 K for a $Hg_{0.065}Ba_2CuO_x$ sample, which is superconducting at 95 K.The thermal behaviour of the lattice parameters a (Å) and c (Å) could be calculated from the fitting to the quadratic polynominal equations

$$a(T)/\text{Å} = 3.869 + 1.310 \cdot 10^{-5}T + 7.206 \cdot 10^{-8}T^2 - 6.998 \cdot 10^{-11}T^3$$

$$c(T)/\text{Å} = 9.496 - 9.942 \cdot 10^{-6}T + 3.690 \cdot 10^{-7}T^2 - 1.817 \cdot 10^{-11}T^3$$

We also obtained $V(T)/\text{Å} = 142.165 + 1.709 \cdot 10^{-5}T^2 - 1.667 \cdot 10^{-8}T^3$ for the volume.

The room-temperature lattice parameters are higher than the results obtained by Wagner *et al.* [2], but they found higher lattice parameters in oxygen-underdoped Hg-1201 samples with low T_c.

Oxygen doping is a traditional way to control the superconducting critical temperature T_c of high-temperature superconductors and, since the discovery of Hg-1201, many efforts have been devoted to its annealing [2, 12]. In our single-step preparation route, no special care was devoted to the oxygen content, except that the samples were prepared in $P_{O_2} = 1$ atm. However, oxygen underdoping does not seem to be possible in our case, as demonstrated by the ρ *vs.* T dependence and $T_c = 95$ K in Fig. 3. Accordingly, we conclude that this is an effect of the low mercury content.

The thermal behavior compares favorably with the data in [2] if shifted by a constant value (Fig. 4), so that the mean thermal expansion coefficients α are quite similar.

It has already been pointed out [13] that the thermal expansion coefficient α is the key measure to obtain C_v from C_p measurements [3]; a good calculation can be obtained from

$$C_v = C_p - \alpha^2 VTK$$

where K is the bulk modulus and V the molar volume.

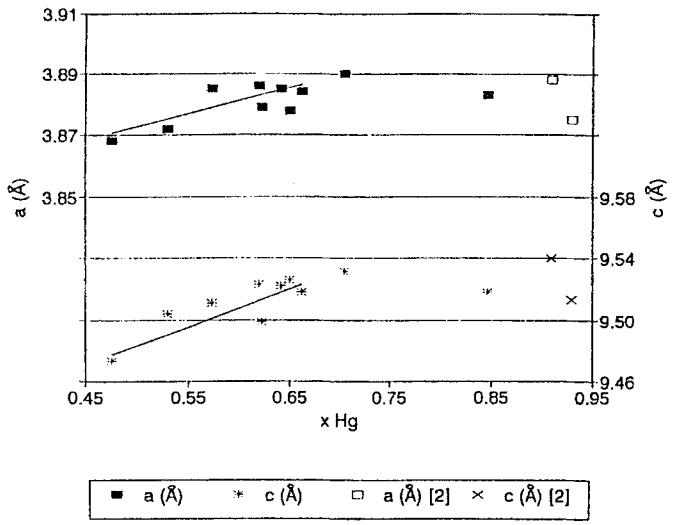

Fig. 3 Resistivity curve of a Hg-1201 single-phase sample

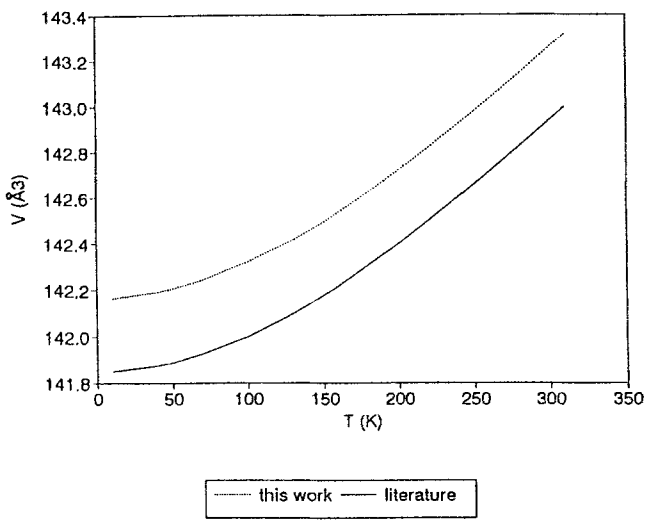

Fig. 4 Comparison of thermal dependence of atomic volume in this work (dashed line) and literature data (continuous line) [2]

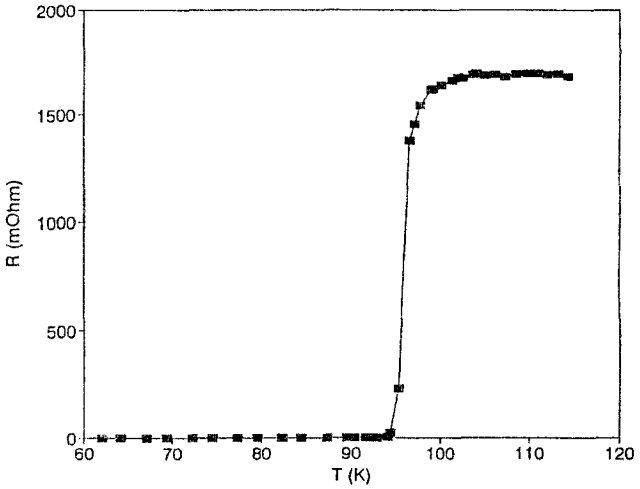

Fig. 5 Behavior of the lattice parameters *a* and *c* of Hg-1201 as a function of mercury content

As referred to previously, copper may replace Hg in its lattice position at least to a small extent [2], but it seems difficult for copper to replace all mercury up to deficiencies of 30% and more, as in our samples, without the appearance of secondary phases. Thus, we have investigated single phases of Hg-1201 with different mercury contents. Figure 5 presents structural results on samples of Hg-1201 with mercury contents ranging from 0.45 to 0.92 (literature values).

The Figure shows two regimes: the first indicates that the lattice parameters do effectively tend to remain constant with Hg contents of from 1 to about 0.7, suggesting compensations by Cu, while the second, visible at lower concentrations of mercury, seems to suggest Hg vacancies.

We believe that the high superconducting critical temperature T_c that is maintained could be due to a charge-compensating effect.

We conclude that more work has to be done on the mutual influence of oxygen doping and mercury loss on Hg-1201.

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