

Growth of heavily Pb-substituted Bi-2201 single crystals by a floating zone method

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Single crystals of the heavily Pb-substituted Bi-2201 phase were grown to a typical planar shape of $6 \times 3 \times 0.03 \text{ mm}^3$ by using a floating zone method [1]. These crystals with the highest Pb content ever reported are free from any structural modulation as examined by transmission electron microscopy, and the orthorhombic lattice parameters are $a = 5.300(3) \text{ \AA}$, $b = 5.392(3) \text{ \AA}$, and $c = 24.603(5) \text{ \AA}$ ($V = 703.2 \text{ \AA}^3$). Their superconducting properties can be modified within the over-doped region in such a way that the transition temperature, T_c , is raised from 3 K for the as-grown crystals to 23 K by annealing at 550°C for 2 weeks in a vacuum of $\sim 10^{-4} \text{ Pa}$. The out-of-plane resistivity of the as-grown crystals remains metallic down to 20 K, while it becomes semiconductive below 160 K after the annealing.

Keywords : Bi-2201/ Single-crystal/ Floating Zone method/ Pb-Substitution/ Anisotropy

There are three superconducting phases in the Bi-Sr-Ca-Cu-O system the ideal formulas of which are $\text{Bi}_2\text{Sr}_n\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ ($n = 1, 2$ and 3). Among these, the Bi-2201 phase ($n = 1$) has the simplest structure with a single CuO_2 sheet in the fundamental unit, and its chemical stability and flexibility allowed to carry out detailed phase diagrammatic studies, various chemical substitutions, and also single crystal growth. Physically this phase has been considered useful to study the normal state properties over a wide temperature range because of its low T_c .

Of particular interest to us are the remarkable changes in structural and superconducting properties resulting from the addition of another element, Pb. Ikeda et al. [2] reported a wide monophasic range of $0 \leq x \leq 0.5$ and $0.1 \leq y \leq 0.5$ for $\text{Bi}_{2-x+y}\text{Pb}_x\text{Sr}_y\text{Cu}_{1+y/4}\text{O}_z$ and showed, in particular, that the structural modulation disappears in a narrow region near the Pb-solubility limit of $x = 0.4$ at $y = 0.125$. The Pb-for-Bi substitution tended to increase the carrier density, and preparation in an Ar stream of 1 atm was needed to induce superconductivity ($T_c = 14 \text{ K}$) from the high Pb

content of $x = 0.4$.

The present work started aiming at the growth of crystals by floating zone method for various metallic compositions within the monophasic region mentioned above. In particular, it was thought interesting to obtain crystals in the modulation-free region because interpretation of experimental results like photoelectron spectroscopic data related to the band structure will be simplified. It should be noted here that Pb content in the previously reported crystals was rather low ($x \sim 0.1$ [3]). Here we report the growth of large plate-like crystals with the highest Pb content ever reported, which are modulation-free, and also the results of conductivity measurements.

Starting materials, which were Bi_2O_3 , PbO , SrCO_3 , and CuO , were weighed at an appropriate ratio, mixed in an agate mortar, pressed into pellets, and heated at temperatures from 720°C to 840°C over a period of 4 - 5 days in total with several intermittent grindings. The obtained powder was then isostatically pressed into a pair of rods of 6 mm in diameter and 60 mm in length and sintered

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Scope of research

Syntheses of oxide thin films by reactive evaporation and ceramics by solid state reaction and their characterizations are studied. The main subjects are: preparation and characterization of ultrathin films of high- T_c superconductors: investigation of growth mechanism of thin films by in situ reflection high-energy electron diffraction: phase diagram of Bi_2O_3 - SrO - CaO - CuO system: growth and characterization of single crystals of Bi-Sr-Ca-Cu-O system: preparation and observation of dielectric properties of ferroelectric thin films: growth and characterization of single crystals of $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$: scanning tunneling microscope observation of surface structures and electronic states of metallic oxide thin films



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Figure 1. Cleaved piece of single crystal.

subsequently at 840 °C for 24 h in air. A molten zone was formed between the pair of rods by infrared irradiation, and the zone was passed through the feed rod at a rate of 5 to 0.3 mm/h. During this growth process the two rods were counter-rotated at 30 rpm. The atmosphere was the air. Single crystals were taken mechanically from the grown ingot.

We could successfully obtain large high-quality single crystals from the initial composition of $\text{Bi}_{1.74}\text{Pb}_{0.38}\text{Sr}_{1.88}\text{CuO}_{6+\delta}$. The single crystal flake with large and plane surface parallel to the ab plane is shown in Fig. 1. The composition of the crystals was determined by fluorescence X-ray analysis to be $\text{Bi}_{1.80}\text{Pb}_{0.38}\text{Sr}_{2.01}\text{CuO}_{6+\delta}$.

The electron diffraction observation revealed that the structural modulation was absent as expected from the high Pb content. The four circle X-ray diffraction measurements showed the orthorhombic structure with lattice parameters of $a = 5.300(3)$ Å, $b = 5.392(3)$ Å, $c = 24.603(5)$ Å, and $V = 703.2$ Å³.

Typical temperature dependences of the in-plane resistivity, ρ_{ab} , and the out-of-plane resistivity, ρ_c , are shown in Figs. 2(a) and 2(b), respectively. T_c was 3 K for the as-grown crystal, while it was raised to 23 K by annealing at 550 °C for 2 weeks in a vacuum of $\sim 10^{-4}$ Pa. This is along an experimentally observed tendency for both the 2201 and 2212 phases that annealing in vacuum reduces oxygen content in the double $\text{BiO}_{1+\delta}$ layers and thereby raises T_c . As shown in Fig. 2(b), ρ_c remains metallic down to near T_c for crystals annealed for relatively short times. Experimentally, Pb-free 2201 crystals have a typical ρ_c of 1 Ωcm at room temperature and its T -dependence remains semiconductive down to T_c [4]. It is known that substitution of La^{3+} for Sr^{2+} also reduces the carrier density and raises T_c [5]. The La-substituted crystals show one-order higher ρ_c at room temperature, and the semiconductive temperature dependence, $|d\rho_c/dT|$, is enhanced [5]. On the other hand, according to Wang et al. [3], a Pb-substituted crystal with $x \sim 0.1$ exhibits metallic behavior down to 80 K, below which ρ_c upturns. In contrast with these cases, an almost complete metallic T -dependence of ρ_c was observed for our as-grown crystals. It is now clear that the present heavy Pb-for-Bi substitution did increase the carrier density to the highest degree ever reported for single crystals.

From the proximity in ionic radius between Pb^{2+} and Bi^{3+} we assume that it is Pb^{2+} rather than Pb^{4+} that substitutes

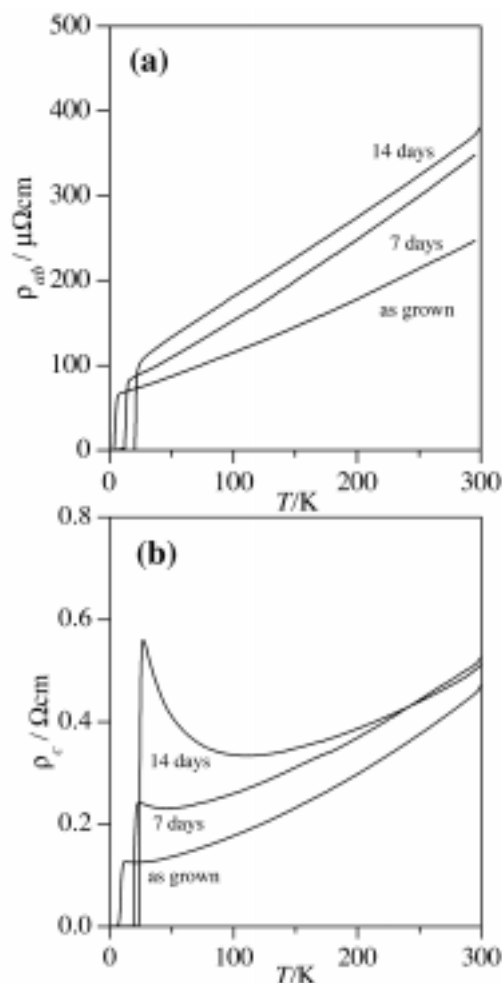


Figure 2. Temperature dependence of the in-plane resistivity (a) and the out-of-plane resistivity (b) of the as-grown and annealed crystals.

for Bi^{3+} . The (Bi, Pb)-O layers become atomically flat in modulation-free crystals as first reported by Ikeda et al. [2]. The flatness should increase the $(\text{Bi}^{3+}, \text{Pb}^{2+})$ 6s - O^{2-} 2p overlap and, thereby, lower the out-of-plane resistivity. We thus conclude that the Pb^{2+} -for- Bi^{3+} substitution makes the (Bi, Pb)-O layers more conductive. In addition to the flatness effects mentioned above, there is another factor which should be taken into consideration. If the energy difference between the Pb^{2+} 6s and the O^{2-} 2p orbitals is smaller than the difference between the Bi^{3+} 6s and the O^{2-} 2p orbitals, the relevant electronic band might become even more broadened. A detailed band structure calculation is desirable.

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