Review

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Review Paper

Floating Zone Growth of Pure and Pb-Doped Bi-2201 Crystals

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Abstract: In this review, we summarize recent progress in crystal growth and understanding the influence of crystal structure on the superconductivity in pure and Pb-doped $Bi_2Sr_2CuO_y$ (Bi-2201) materials belonging to the overdoped region of high temperature cuprate superconductors. The crystal growth of Bi-2201 superconductors faces challenges due to intricate materials chemistry and lack of knowledge of corresponding phase diagrams. Historically, a crucible-free floating zone method has emerged as the most promising growth approach for these materials, resulting in high-quality single crystals. This review outlines the described in the literature and the authors' synthesis endeavors, encompassing Pb-doped Bi-2201 crystals, detailed structural characterization of as-grown and post-growth annealed samples, and highlights optimal growth conditions that yield large-size, single-phase, and compositionally homogeneous Bi-2201 single crystals.

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1. Introduction

It is commonly believed that superconductivity is more conventional in overdoped cuprates [1–3]. Transport and spectroscopic studies suggest that the non-superconducting ground state is more ‘normal’ and the superconducting (SC) state exhibits Bardeen–Cooper–Schrieffer (BCS) *d*-wave features [4]. However, recent experiments have shown unconventional behavior in strongly overdoped cuprates in both the normal [5,6] and superconducting states [7,8]. $Bi_2Sr_2CuO_y$ (Bi-2201) cuprate came into a focus due to the recent investigations unraveling its unique features: the presence of pseudogap in the overdoped side of the electronic phase diagram, which questions the scenario of the pseudogap phase crossing the superconducting dome [9] and Lifshitz transition from a hole-like Fermi surface topology to an electron-like Fermi surface topology occurring at the doping level where the sample becomes non-superconducting [10]. Besides, circular and linear photogalvanic measurements transition revealed that the pseudogap regime in both Bi-2201 [11] and Bi-2212 [12] families marks a phase transition associated with the development of chiral and inversion symmetry breaking. Reducing the symmetry of a superconducting material modifies the properties of the superconducting states, e.g. recently, a spin texture with nonzero spin polarization was found in Bi-2212 [13], which could be caused either by an absence of any inversion center in the structure or a local symmetry breaking, due to structural distortions typical for cuprates. Several other investigations of the closely related doped Bi-2212 system also raise doubts regarding the centrosymmetry of the crystal structure [12,13].

The superconducting Bi-2201 has relatively simple crystallographic structure possessing only one the copper oxide block in the unit cell as well as simple electronic band structure, providing an excellent platform for comparing density functional theory calculations with direct band-structure probes. In opposite, two-layered (n=2, Bi-2212) or multi-layered (n=3, Bi-2223) compounds have a significant band structure splitting [14], which complicates the interpretation of angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM) results.

From a physical point, it seems to be rational to examine relations between superconductivity and pseudogap in low T_c cuprates. As it is simplified a proper disentanglement of superconducting and pseudgap features, because thermal fluctuations become much less pronounced once the temperature is approaching 0 K. Therefore, the pure Bi2Sr2CuOy compound was suggested to be a promising model system. And, in turn, the angular-dependent magnetoresistance [15] and intrinsic tunneling [16] studies in Bi-2201 cuprate with $T_c \sim$ 3-4 K reveals the large disparity of superconducting and pseudogap scales.

It is known that by partial substituting Bi by Pb in Bi-2201, together with annealing under different conditions, the samples can be pushed to the overdoped and heavily overdoped regions to even become non-superconducting. However, doping does not change the value of T_c in a systematic way, rather it strongly depends on synthesis conditions and different synthesis protocols may result in samples with different T_c. Apparently, the floating zone crystal growth results in high-quality single crystals of undoped and Pb-doped Bi-2201 with a homogenous composition distribution along the crystal ingot [17,18] but is quite time-consuming. Therefore, there are only a few reports about the crystal growth by this technique and only a few structural works on such crystals available in the literature since the 80's. In this review we are going to particularly focus on the floating zone growth of Pb-doped Bi-2201 crystals and compare crystal structures of two heavily doped as-grown and post-growth annealed samples with corresponding T_c = 3 K and 23 K.

2. State of the art

2.1. Crystal growth

The first pure Bi-2201 samples were prepared by flux technique, using either self-flux (CuO-based flux) [19] or KCl-flux [20]. Unfortunately, as it was recognized later, the flux-prepared samples always suffer from several drawbacks [21]: (1) crucible material contamination due to the melt corrosion at high temperatures; (2) flux inclusions (mainly CuO) in as-grown samples; (3) small samples (< 2 mm) in (a,b)-plane while typical thickness along c-axis is less than 0.1 mm; (4) mechanical detaching of crystals from a solidified melt causes often a sample damage and (5) a small yield of the growth. Moreover, a possible K and Cl pollution has to be considered for KCl-flux grown samples. Another dramatic problem is that flux-prepared crystals show often poor reproducibility of superconductivity [21]. For example, Bi-2201 samples were fabricated by CuO self-flux technique in $Zr(Y)O_2$ (YSZ), Al_2O_3 and Au containers in Sonder et al [22]. The superconductivity in samples grown in alumina container was not well reproducible. A few of crystals demonstrated a broad SC transition by resistivity measurements, but none of them showed a well-defined SC transition by magnetization measurements. On the other hand, the superconductivity in Bi-2201 samples fabricated in either YSZ or Au containers was well reproducible. And both resistivity and magnetization measurements proved a presence of bulk superconductivity. The authors carried out a very accurate chemical analysis of sample content using spark-source mass spectroscopy. Obviously, Al was detected in Bi-2201 samples prepared in Al_2O_3 container but at very low levels of 10-50 ppm. Concurrently, samples grown in YSZ crucibles had remarkably higher concentrations of both Zr (20-70 ppm) and Y (50-120 ppm). All crystals fabricated in Au container had no visible sign of Au pollution (Au content < 5 ppm) according to this chemical analysis. The effect of Al pollution on superconductivity in Bi-2201 crystals has not been yet well understood. Besides these drawbacks, all flux prepared crystals have been rather small, typically $4{\times}4{\times}0.02$ mm^3 in size [22].

A crucible-free floating zone (FZ) method allowed one to overcome nearly all of the abovementioned drawbacks of the flux technique. This method was successfully used for the crystal preparation of many other high-T_c cuprates like, for example, $(La,Sr)_2CuO_4$ [23] and $Bi_2Sr_2CaCu_2O_y$ [24]. However, the first Bi-2201 samples grown by FZ technique were rather non-superconducting [25]. All attempts to improve superconducting properties by post-growth heat treatment in oxygen/argon flow were failed. The first superconducting [18] and bulk Bi-2201 samples suitable even for inelastic neutron measurements [21] were prepared only in the late 90's. Nevertheless, it was noted that T_c varies from sample to sample, and some crystals collected from the same ingot failed to show any superconductivity although other samples were superconducting. The authors [21] could not find and difference between these crystals either in composition (by EDX) or in their powder XRD patterns. The similar effect was observed on FZ grown $PrBa_2Cu_3O_{7-y}$ samples [26]. From the growth point of view, the FZ fabrication of undoped and Pb-doped Bi-2201 samples seem to be very similar. Consequently, we will mostly discuss the intricate details of the FZ growth for lead-doped samples. Also, we do not touch both the CuO-flux [27] or FZ growth of La-doped Bi-2201 crystals due to the composition inhomogeneity problems in as-grown ingots [28].

2.2. Crystal structure

In terms of the crystal structure, Bi-based cuprates are intergrowths of two BiO sheets with n (n = 1, 2, 3...) copper oxide perovskite-like layers [17]. The first member (n = 1) is named after its nominal stoichiometric composition Bi-2201. Although the early structural studies of the superconducting Bi-2201 from the powder XRD data have suggested a tetragonal structure with the space group *I*4/*mmm* and lattice parameters a_t = 3.8097(4) Å and c_t = 24.607(3) Å [29], the subsequent single crystal X-ray diffraction (SCXRD) and electron diffraction studies revealed that it possesses an orthorhombic structure with inequivalent *a* and *b* axes, which may be accompanied by a minor monoclinic distortion (Mironov et al [30]). While the in-plane lattice anisotropy is absent in Bi-2212 (n = 2) and CCOC ($Ca_{2-x}Na_xCuO_2Cl_2$) compounds, it was found to be important for e.g. YBCO and $La_{2-x}Sr_xCuO_4$ materials [31]. The space group *Cccm* is typically suggested for the parent Bi-2201 in the literature (Torardi et al [32], Leligny et al [33]), with lattice parameters of approx. $a_t\sqrt{2}\times c_t\times a_t\sqrt{2}$, often the space group denoted as *Amaa* or *Bbmb*. In non-conventional settings the orthorhombic long axis sets to be co-directional with the pseudo-tetragonal one. Ito et al [34] has reported the first SCXRD crystal structure solved from a heavily Pb-doped Bi-2201 crystal grown by floating zone growth technique. At the Pb/(Bi+Pb) ratio 0.15 it found to possess the space group *Cccm* with the lattice parameters a = 5.392(3) Å, b = 24.603(5) Å, c = 5.300(3) Å, V = 703.2 (5) Å^3. [34]

Although most authors consider *Amaa* or its subgroup *A*2/*a* for the structure description of undoped Bi-2201, see Torardi et al [32], Leligny et al [33], Mironov et al [30], it is worth to note that several cases of closely related non-centrosymmetric structures have been also known, e.g. Tarascon el al [35] has reported structures of modulation-free non-superconducting $BiPbSr_2MO_y$ phases (M = Co, Mn, Fe) possessing the space group *A*2*aa*, Gao et al [36] proved the space group *A*2*aa* for the average structure of a Pb-doped single layer $Bi_2Sr_{2-x}Ca_xCuO_6$ cuprate and the *Aa* symmetry of the satellite diffraction pattern.

An average crystal structure of Bi-2201 possess single sheets of corner-sharing CuO_4 units in which each copper atom has two additional oxygen atoms positioned above and below the sheet to form an axially elongated (Jahn-Teller-distorted) octahedron. These Cu-O planes are separated by Bi-O and Sr-O layers formed by distorted MO_6 edge-shared octahedra. Cu-O layers in the superconducting orthorhombic Bi-2201 phase may be buckled. It is known that local lattice distortions produced by chemical inhomogeneity can reduce the value of T_c in a systematic way: the larger the Cu-O plane buckling angle, the lower the T_c. Nevertheless, T_c of superconducting Bi-2201 species varies, and these variations are sensible to multiple internal structural features. Buckling alone is not sufficient to characterize properties associated with superconductivity – thus, the Raveau phase is found to contain periodic crystallographic shears interrupting the connections of the flat CuO_2 planes [37], leading to insulating behavior [38]. In contrast, superconducting Tl-2201 (T_c around 90 K) has a tetragonal structure with nearly perfectly flat Cu-O layers and a slight buckling in the Tl-O and Ba-O layers [32].

In the literature, the off-stoichiometric Raveau phase, exhibiting superconductivity, is regularly denoted as Bi-2201 too, leading to a notable degree of confusion. It is worth noting that the composition of the orthorhombic Raveau phase is always off-stoichiometric with the partial substitution of Bi for Sr, it forms $Bi_{2+x}Sr_{2-x}CuO_y$ solid solution with $0.1\,5\leq x\leq 0.4$ [39]. Structurally the perfectly stoichiometric Bi-2201 compound is insulating and has a monoclinic unit cell with a = 24.451(5) Å, b = 5.425(2) Å, c = 21.954(5) Å and β = 105.41(1)^0 [37], and sometimes named a "collapsed" Bi-2201 since its c_t axis is 1 Å shorter than those of superconducting Bi-2201 . The structure is derived from that of the pseudo-tetragonal 2201 phase by a periodic crystallographic shear parallel to the c_t axis. Periodic slabs of 2201 with a thickness of eight octahedra are then formed [37], as shown by HRTEM observations.

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A well-known structural feature in the Bi-based high-T_c superconductors is an incommensurate modulation, appearing due to metal atoms as well as oxygen disorder in Bi-O and Sr-O layers or (CuO_2) planes, caused by the mismatch of perovskite and rock salt blocks of the structure. Despite the close resemblance in average structures between 2201 and 2212 ($Bi_2Sr_{2-x}Ca_xCuO_6$) systems, a distinct difference exists in the modulation type in these structures. While the modulation in the 2212 phase has a wave vector of $0.21a^*$, the modulation in the 2201 phase has been described by two wave vectors with $q_1 = 0.21a^* + 1/3c^*$ and $q_2 = 0.21a^* - 1/3c^*$ (sp.gr. *Amaa* was used in the original works). An influence of Pb substitution on the satellite pattern is also evident: doping of the 2201 phase leads to a disappearance of the satellites in the X-ray pattern, while Pb doping of the Sr/Ca 2212 phase gives a diffraction pattern with two different q vectors both in the a^* direction [40]. Another approach was suggested by considering the Bi-containing mixed oxide structures as composites [41] with the oxygen in the Bi-O layer forming the second sublattice, whereas all other atoms belong to the first one. Refinement of the composite structure was taken by Yamamoto et al.[42], the correlation was revealed between the q vector and the extra oxygen content within the Bi-O layer.

3. Results

3.1. Floating zone crystal growth of Pb-doped Bi-2201 at IFW Dresden

The large-size lead-doped Bi-2201 crystals have been prepared by crucible-free FZ method in 1997 for the first time [18]. Prior to the growth as-sintered feed rod was pre-melted at a fast rate of 25-27 mm/h in infrared (IR) image furnace in order to obtain a high dense rod with density above 90% of the crystal density. For the feed rod preparation, Bi_2O_3, PbO, $SrCO_3$ and CuO powders of, at least, 3N purity were used as starting materials. A number of feed rod compositions were investigated. Initial powder mixture was mixed in ethanol and fired at 720-840 C for 24 h in air. The rods were pressed at 1 kbars by cold isostatic press and finally fired at 840 °C for 24 h in the air. The best feed rod composition was detected to be $Bi_{1.74}Pb_{0.38}Sr_{1.88}CuO_y$. The crystal growth was initiated by forming a molten zone between the feed and seed rods using IR heating, and the zone was passed through the feed rod at a rate of 5.0 to 0.3 mm/h [18].

Large size and bulk $Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$ single crystals were grown at IFW-Dresden in a similar way. The 4-mirror type image furnace produced by CSI (Japan) equipped with 4x300 W halogen lamps was used for the growth, Figure 1. We have found that the using of pre-melted feed rod does play an important role for a stable growth run because liquid penetration onto a feed rod was strongly suppressed in this case [21]. Therefore, for high dense pre-melted feed rod a stable molten zone (MZ) could be maintained over a long lasting experiment (over 1-2 days). In contrast, using of low dense as-sintered rods with density less than 75% always terminated a FZ growth due to the dramatic liquid penetration. Thus, a straight, high dense and equal-diameter pre-melted rod is crucial to stabilize a MZ for long lasting growth. Also, similar to undoped Bi-2201, a high temperature gradient (~150-300 °C/cm) in a hot zone generated by correctly focused halogen lamps is needed to maintain a stable molten zone. Long size (about 10 mm in length) pre-melted rod was cut into two pieces, and the shorter piece (~ 2 cm in length) was utilized as a seed and the longer one as a feed rod. Both feed and seed rods were coaxially mounted on upper and lower shafts inside a transparent quartz tube. The used O-ring sealing is gas tight and protects a growth atmosphere from air humidity. Slow growth rates of 0.5-1.0 mm/ were applied in order to get a faster grain selection. Both feed and seed rods were counter rotated (15-20 rpm) to provide a homogeneous temperature distribution in radial direction. The bulk Pb-substituted Bi-2201 crystals with the actual composition $Bi_{1.8}Pb_{0.38}Sr_{2.01}CuO_y$ were successfully fabricated by using the CSI image furnace with infrared heating. The growth was performed in $Ar/O_2 = 90/10$ gas mixture, the actual pulling rate was 1.0-0.8 mm/h. As-grown samples were non-superconducting above 4 K from the magnetization measurements, and demonstrated a superconducting transition at T_c~22-23 K after a post-growth heat treatment under vacuum conditions [18].

The Pb-doped Bi-2201 single crystals cleaved by sharp scalpel from as-grown ingot are depicted on Figure 2 (left). The biggest samples had dimensions up to $15 \times 4 \times 3$ mm^3 with a clear (010) cleavage

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plane. The weak PbO and Bi_2O_3 evaporation from MZ was detected during a growth. The boiling points of PbO and Bi_2O_3 oxides are 1480 °C and 1890 °C, respectively. The evaporated material deposits on inner wall of quartz tube forming a slightly yellowish thin layer. Therefore, the IR heating was not affected by it. Therefore, there was not need to increase a lamps power and, in turn, the MZ remained stable over the growth.

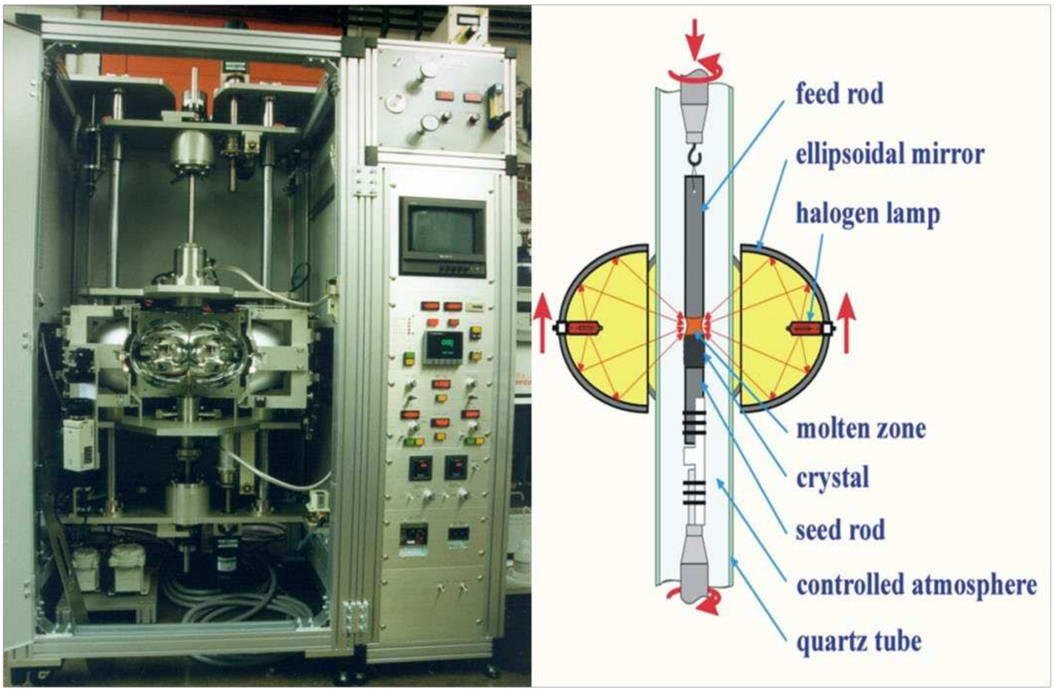

Figure 1. A sketch of the 4-mirror type image furnace with IR heating installed at IFW Dresden (produced by CSI, Japan). Reproduced from ref. [17], with permission from the Springer International Publishing, copyright 2016 (not received yet).

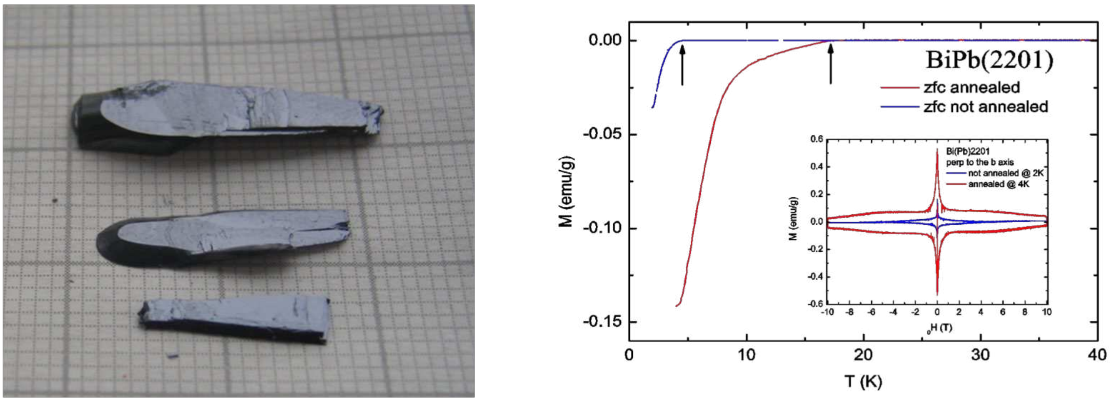

Figure 2. (Left) As-grown Pb-doped Bi-2201 crystals. (Right) Superconductivity in as-grown and Ar-annealed Bi(Pb)-2201 crystals. Arrows indicate T_c onset. Reproduced from ref. [17], with permission from the Springer International Publishing, copyright (not received yet).

Typically, $Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$ samples with thickness of 2-3 mm along c-axis show broadening of neutron rocking curves due to weak shoulders around a few Bragg peaks reflecting the co-existence of slightly misoriented grains. The mosaicity of these crystals was found to be about 2-3°. In contrast, crystals with the thickness of 0.3-0.5 mm along c-axis demonstrate better mosaicity of about 0.5-0.7° [17].

As-grown lead-substituted Bi-2201 crystals are usually non-superconducting above 3 K but post-growth heat treatment in vacuum dramatically enhances T_c up to 22-23 K (Figure2, right). Annealing conditions and effects of heat treatment on superconductivity and material stability of $Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$ crystals are summarized in Table 1 [17]. Since the substitution of Bi^{3+} with Pb^{2+} is believed to generate holes in a sample, lead doping makes the Bi-2201 compound to be heavily overdoped.

Table 1. Annealing conditions and results on $Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$ superconductivity. Reproduced from ref. [17], with permission from the Springer International Publishing, copyright 2016. (not received yet).

Crystal composition	Annealing atmosphere	Annealing time	Superconductivity, T_c (K)[1]	Comment
$Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$	as-grown	0 days	3 K	stable in air
$Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$	450 ^{0}C in O_2	7 days	non-superconducting	stable in air
$Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$	450 ^{0}C in Ar	10 days	13 K	stable in air
$Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$	450 ^{0}C, 10^{-5} mbar	7 days	17 K	stable in air
$Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$	550 ^{0}C, 10^{-5} mbar	5 days	23 K	non-stable in air
$Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$	650 ^{0}C, 10^{-5} mbar	3 days	no measurement	decomposed

[1] T_c was determined from magnetization measurements.

The low-temperature superconductivity does vanish in as-grown samples after annealing in the oxygen flow (at least, T_c is below the low temperature limit 2 K of our experimental facility). In contrast, annealing of as-grown lead-doped Bi-2201 samples in vacuum (~ 10^{-5} mbar) at 550 °C for 7 days increases T_c up to 22-23 K. This is a direct hint for extra oxygen expel from as-grown Pb-doped Bi-2201 samples reflecting a reduction of sample doping from heavily overdoped to slightly overdoped. By adjusting the annealing atmosphere and temperature, the superconductivity transition temperature could be varied between 0 and 23 K. Nevertheless, the lead-substituted Bi-2201 samples became air sensitive after post-growth heat treatment under vacuum conditions above 550 °C. These crystals were completely powdered after keeping on a desk at room temperature for a week. Only crystals annealed either in Ar flow (5N purity) or in vacuum below 450 °C remain stable in air, and have no visible sign of crystal decomposition and retain superconductivity. Thus, the superconductivity in a lead-doped Bi-2201 material is highly sensitive to annealing process and may result in samples with various T_c if the heat treatment was carried out under different conditions [43]. It has been found in the literature that the whole region from slightly overdoped to heavily overdoped samples can be covered by combining the Pb^{2+} partial doping with annealing at reduced atmosphere.

Concerning the effect of lead doping on the structural modulation, it is found that the modulation preserves by the La doping, while the substitution of Pb for Bi acts effectively for a modulation suppression[44]. It was shown by Ikeda et al [45] that structural modulation disappears in a narrow range near the Pb-solubility region of $x= 0.4$ at $y = 0.125$ in $Bi_{2-x}Pb_xSr_{2-y}CuO_z$. .

3.2. SCXRD investigations on Pb-doped Bi-2201

The majority of previous structural characterization works for the Bi-2201 family of cuprates were performed on crystals grown from off-stoichiometric oxides mixtures, therefore the “best” crystals chosen for SCXRD might not always be representative of the bulk. Floating zone crystal growth, in opposite, guarantees a homogenous composition distribution along a crystal ingot [17,18], which is beneficial for the reproducibility of SCXRD analysis, too. Unfortunately there are only few reports about the crystal growth by this technique and, consequently, a few structural works on such crystals available in the literature since the 80’s [34]. In this section, we thoroughly analyzed centrosymmetry as well as modulation suppression on two heavily Pb-doped Bi-2201 crystals, before and after post-growth annealing.

Single crystal X-ray diffraction data acquisition was accomplished on a Bruker D8 Venture (MoKα $\lambda = 0.71073$ Å) equipped with a PHOTON 100 CMOS detector. The measurements were performed at room temperature. Indexing was performed using APEX3 software [46]. Data integration and absorption corrections were performed using the SAINT and SADABS [46,47] software, respectively. Crystal structure was solved by dual-space methods implemented in the SHELXT [48] program and refined by full-matrix least-squares method on F^2 with SHELXL[49]. The composition of the crystal was taken from EDX analysis.

Generally, our SCXRD data confirm the average crystal structure of Pb-doped Bi-2201 described in the literature. SCXRD reflections can be indeed indexed in a *C*-centered orthorhombic cell with very close values of lattice parameters $a = 5.388(2)$ Å, $b = 24.608(1)$ Å, $c = 5.279(2)$ Å (a non-annealed crystal with $T_c = 3$ K, further denoted as OD3K) or $a = 5.3947(6)$ Å, $b = 24.605(3)$ Å, $c = 5.2786(6)$ Å (an annealed crystal with $T_c = 23$ K, further denoted as OD23K). A notable feature of the OD23K crystal is a very weak incommensurate modulation with $q \approx 0.21\ c^*$, clearly seen in 0*kl* reciprocal layers (see Figure 3). For a comparison, the OD3K crystal demonstrate rather thin diffuse streaks along a^* instead of well-defined spots of satellite reflections, Figure 4. This modulation in OD23K cannot be entirely associated with the post-annealing, it is present also in the sample before annealing. The mismatch between the BiO-slab and the copper oxide perovskite block cannot be eliminated by Pb-doping alone, and the observed modulation is evidently a residual feature. The *q*-vector value is close to those reported by Gao et al [36] for a Pb-doped single layer $Bi_2Sr_{2-x}Ca_xCuO_6$ cuprate as well as to those previously reported for undoped Bi-2212 [50] ($q \approx 0.21\ a^*$, sp.gr. *Amaa* was used in the original works). In opposite, some literature testifies a full disappearance of the satellite patterns in heavily Pb-doped Bi-2201 [34,45]. In in the following discussion we show that these weak reflections can be convincingly described in a non-centrosymmetric space group *Ccc*2.

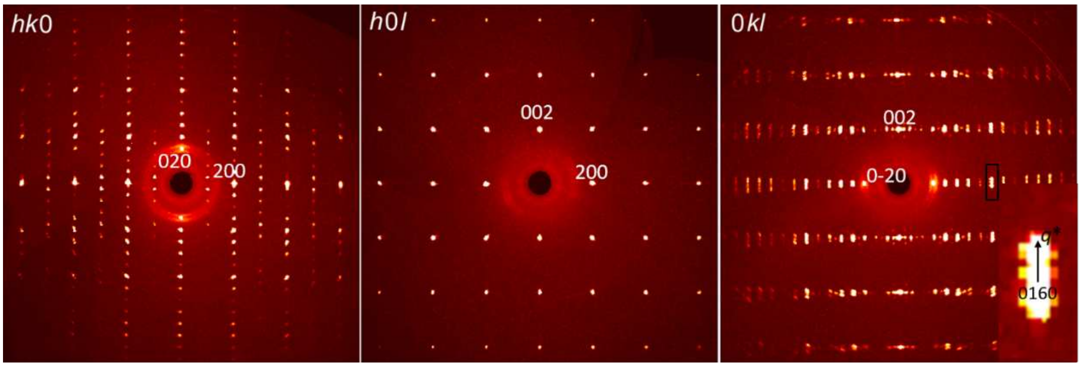

Figure 3. Recalculated reciprocal layers *hk*0, *h*0*l* and 0*kl* for an annealed OD23K crystal with $T_c = 23$ K, and composition Pb:Bi:Sr:Cu = 0.35(3):1.69(8):2.01(9):1, Pb/(Bi+Pb) ratio is 0.17. A disappearingly weak incommensurate modulation with $q \approx 0.21\ c^*$ preserves even at very high Pb concentrations in Pb,Bi-2201, see the inset.

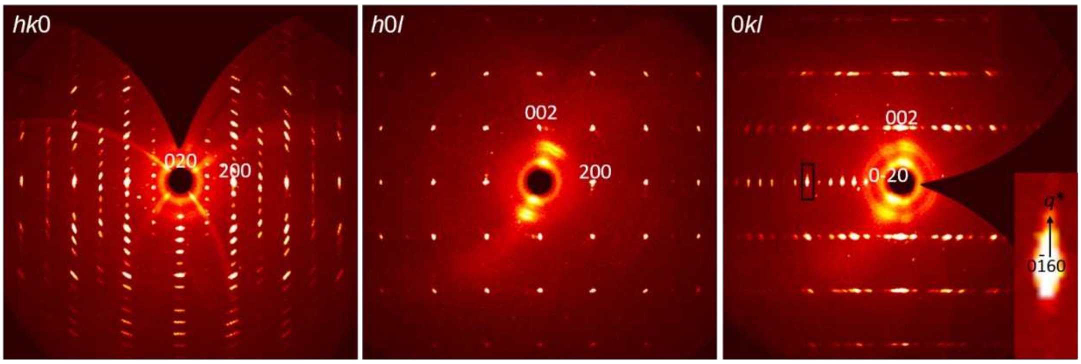

Figure 4. Recalculated reciprocal layers *hk*0, *h*0*l* and 0*kl* for a non-annealed OD3K crystal with $T_c = 3$ K, and composition $Bi_{1.6}Pb_{0.4}Sr_{2.05}CuO_y$ Pb:Bi:Sr:Cu = 0.4:1.6:2.05:1, Pb/(Bi+Pb) ratio is 0.2.

The Pb,Bi-2201 structure can be solved and refined either in the centrosymmetric *Cccm* or in non-centrosymmetric *Ccc*2 space group. It is worth noting that E-statistics indicate that the structure is rather non-centrosymmetric, Sheldrick's $|E^2 - 1|$ criterion is 0.769, see Figure 5, data for the OD23K crystal.

We tested both *Cccm* and *Ccc*2 solutions and ascertained that the positions of the metal atoms Bi, Sr, and Cu found by *ab-initio* structure solution by SHELXT are basically equivalent in both space groups. However, refined anisotropic temperature factors (ADP) for the metal atoms as well as crystallographic coordinations of Bi/Pb by O atoms are clearly different. The structure solution in space group *Cccm* showed structural arrangement very similar to one described previously for the parent 2201 phase, with ribbons of strong Bi-O bonds, and splitting of the oxygen site in the Bi plane. Moreover, the Bi atoms in this model had very large anisotropic factors along the *c*-axis.

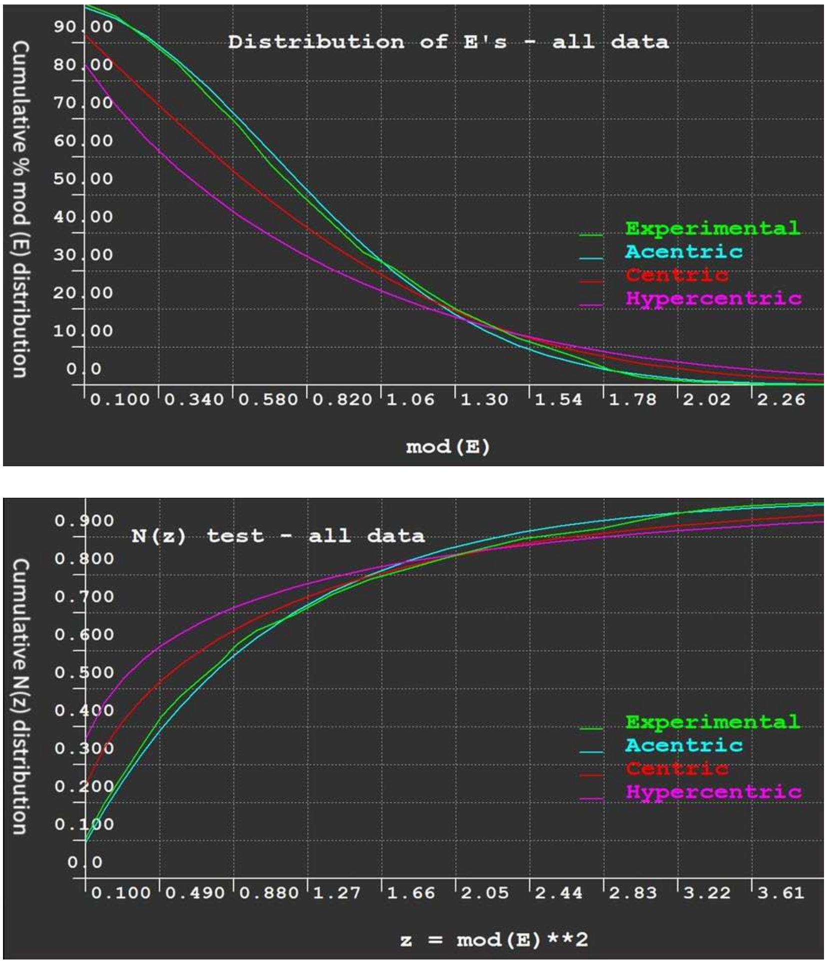

Figure 5. E-statistics indicate the structure of Pb-doped Bi-2201 is non-centrosymmetric. The probability that the structure is centrosymmetric is only 18.5 %. Sheldrick's $|E^2 - 1|$ criterion is 0.769 (Ideal values CENTRIC = 0.968, ACENTRIC = 0.736).

Lowering symmetry to *Ccc*2 and the refinement of this model resulted in $R_1 = 4.78\%$ and reasonable ADP along the *c*-axis. The atomic coordinates, temperature factors, and site occupancies for the Bi-2201 crystal together with the details of the refinement are listed in Tables S1-S3. As can be seen from these tables, the stereochemistry of the various ions is as expected for this structure type (Figure 6). In distinction to Y. Ito et al [51], where the Pb dopant was placed in both Bi and Sr sites, we assume that the Sr sites are occupied predominantly by Sr, whereas Pb/Bi sites are mixed occupied. Since scattering powers of Pb and Bi are almost equal for wavelengths which are not close to an absorption edge, these atoms cannot be distinguished by conventional X-rays. The experimental composition measured by EDX and averaged over all measurements found to be Pb:Bi:Sr:Cu =

0.35(3):1.69(8):2.01(9):1, Pb/(Bi+Pb) ratio is 0.17, thus, Cu oxidation state can be estimated as +2.21, providing ideal oxygen composition. SCXRD refinement reveals that the Pb/Bi site may be slightly underoccupied, as compared to the EDX data. There is no extra-oxygen position found within the Bi-O layers, in contrast to the undoped Bi-2201, e.g. Mironov et al [30].

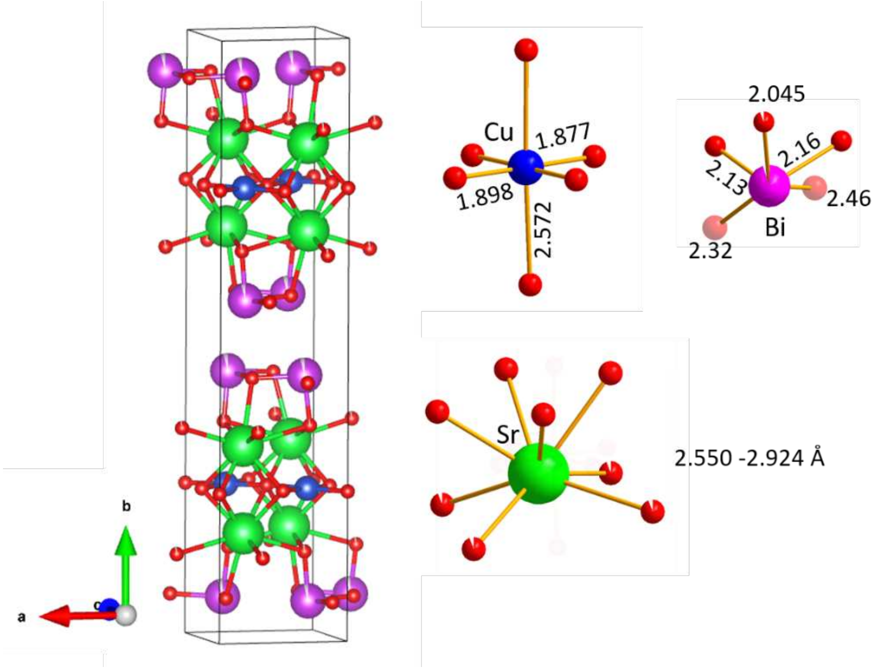

Figure 6. Crystal structure and coordinations of heavy atoms in Pb-doped Bi-2201.

The crystal structure of a non-annealed OD3K crystal was also refined in the space group *Ccc*2 using 12508 reflections measured (3.318° ≤ 2Θ ≤ 61.82°), 1070 unique (R_{int} = 0.1170, R_{sigma} = 0.0462) in all calculations. The final R_1 was 0.0852 (I > 2σ(I)) and wR_2 was 0.1868 (all data). For comparison, the refinement in the centrosymmetric space group *Cccm* has converged to R_1 = 0.1040 (I > 2σ(I)) and wR_2 = 0.2298 (all data). The atomic coordinates, temperature factors, and site occupancies for the OD0K crystal together with the details of the refinement are listed in Tables S4-S6.

In the table 2, we put together different structural models proposed in the literature for the doped Bi-2201 and Bi-2212 compounds.

Table 2. A comparison of models reported for the average structure of superconducting doped Bi-2201 and Bi-2212.

	Present study	Ito et al [34]	Imai et al [52]	Gao et al [40]	Gao et al [36]	Tarascon et al [53]
Composition	$(Bi,Pb)_{1.902}Sr_2CuO_{5.885}$	$Bi_{1.82}Pb_{0.32}Sr_{1.84}CuO_6$	$Bi_2Sr_{1.60}Ca_{0.40}CuO_6$	$Bi_{2.28}(Sr,Ca)_{1.72}CuO_6$	$Bi_{2.14}Pb_{0.19}Sr_{1.11}Ca_{0.43}CuO_6$	$Bi_{1.2}Pb_{0.8}Sr_{1.5}La_{0.5}CuO_6$
Space group	*Ccc*2	*Cccm*	*Bbmb* (*Cccm*)	*A*2/*a*	*A*2*aa* (*Ccc*2)	*Pnan*
a, Å	5.3947(6)	5.392(3)	5.3826(8)	5.362(2)	5.3312(6)	5.328(1)
b, Å	24.605(3)	24.603(5)	5.376(1)	5.362(1)	5.3686(4)	5.415(1)
c, Å	5.2786(6)	5.300(3)	24.387(7)	24.30(1)	24.365(6)	24.383(1)
R	0.0478	0.048	0.109	0.104	0.105	0.10
R_w	0.112	0.077	0.108	0.111	0.117	0.14

Thus, the substitution of Bi by Pb has yielded the observation of superconductivity in Bi-2201 materials that do not contain extra oxygen within the Bi-O layers, also this suggests a lowering of the oxygen content to 6 per formula unit. The subtle difference between structures with space groups *Ccc*2 and *Pnan* originates in the position of the oxygen atoms with respect to Bi in the Bi-O layers.

4. Summary and conclusions

The crucible-free floating zone method has emerged as the most promising growth approach to grew large size and compositionally homogeneous crystals of pure and Pb-doped Bi-2201. The FZ grown Bi-2201 samples are always much larger and thicker along the *c*-axis as compared to flux-prepared crystals, and are suitable even for neutron scattering experiments. In contrast to pure Bi-2201, the Pb-doped samples grown by FZ method reproducibly demonstrate superconducting properties after annealing in either vacuum or reduced atmosphere.

Even highly Pb-overdoped Bi-2201 seems to be prone to a weak modulation with $q \approx 0.21\, c^*$, which does not disappear even after the post-annealing. We show that these weak reflections can be convincingly described in a non-centrosymmetric space group *Ccc*2. The origin of non-centrosymmetricity is the position of the oxygen atoms with respect to Bi atoms in the Bi-O slabs. In Pb-doped Bi-2201 cuprates there are no extra-oxygens within the Bi-O layers, in contrast to undoped Bi-2201, e.g. Mironov et al [30]. Superconductivity appears in the non-annealed material with the critical temperature of 3 K and preserves in the annealed one with T_c as high as 23 K.

Supplementary Materials: The atomic coordinates, temperature factors, and site occupancies for the Bi-2201 crystals together with the details of the refinement are listed in Tables S1-S6.

Author Contributions: All of the authors declare that they have participated in the design, execution, and analysis of the paper: Crystal growth, A.M.; SCXRD Investigation, M.R.; Writing – Original Draft Preparation, M.R and A.M; Writing – Review & Editing, B.B.; Project Administration, A.M. and B.B. Authors declare no conflicts of interest.

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