Growth of Bi-(Sr,La)-Cu-O single crystals with the floating-zone technique

J.H.P.M. Emmen[a], V.A.M. Brabers[a], W.J.M. de Jonge[a], M. Nevriva[b] and J. Srámek[b],

[a]Department of Physics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

[b]Institute of Physics, Czechoslovak Academy of Sciences, Cukrovanicka 10, Prague 6, Czechoslovakia.

Abstract

The TSFZ method has been used to grow crystals of the Bi-oxide superconductor of the Bi-$n = 1$ structure. The investigated compositions are $Bi_2Sr_2CuO_{6+z}$, $Bi_{2.3}Sr_{1.7}CuO_{6+z}$, and $Bi_{2+x}Sr_{1.6}La_yCuO_{6+z}$ ($x+y = 0.4$). Except for the stoichiometric composition, the TSFZ experiments yield plate-like crystals of the superconducting R-phase. Superconductivity was only present in La substituted crystals and the T_c could be changed by annealing procedures. A maximum $T_c = 29$ K is found for $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$.

1. Introduction

Of all known superconducting ceramic systems, the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+z}$ ($n = 1,2,3$) family has drawn considerable attention, caused by the fact that this family consists of three superconducting members. While most of the research activities have been focused on the Bi-$n = 2,3$ compounds because of their higher T_c, the Bi-$n = 1$ compound seems equally important since it exhibits the most simple crystallographic structure and enables the study of the normal state properties down to much lower temperatures.

As in many other ceramic superconductors, T_c of the Bi-$n = 1$ phase depends on the hole concentration per Cu atom per CuO_2 layer $pCuO_2$. Generally it is believed that for pure Bi-$n = 1$, $pCuO_2$ must be adjusted in order to optimize T_c [1]. This can be achieved by annealing at elevated temperatures followed by rapid cooling [2,3] or by substitution with cations which have a higher valency. An example of such a substitution is the system $Bi_2Sr_{2-x}La_xCuO_{6+z}$, where T_c increases from 9 K for $x = 0$ to a maximum value of 25 K for $x = 0.4$ [3–5].

Despite the assumed crystallographic simplicity for Bi-$n = 1$ compared with Bi-$n = 2,3$, the crystal growth of this compound is rather complicated. This is caused by the fact that two structures, one superconducting layered phase and one non-superconducting insulating phase, are in thermodynamic equilibrium near the model composition $Bi_2Sr_2CuO_6$. The composition of the non-superconducting phase, also called the collapsed phase [2,6], is $Bi_{17}Sr_{16}Cu_7O_y$ [7]. The superconducting phase (R-phase) is formed by the solid solution $Bi_{2+x}Sr_{2-x}CuO_{6+z}$, with $0.15 > x > 0.4$ [8,9].

Single crystals of Bi-$n = 1$ have been grown with the self flux method. However, due to the high reactivity and the incongruently melting of Bi-$n = 1$, this crystal growth technique has several drawbacks, such as contamination by the crucible material, low homogeneity of the grown crystals and a small yield [6,10,11]. These disadvantages can be circumvented with the travelling-solvent floating-zone (TSFZ) process. Results reported by Matsumoto et al. [12] indicate that the TSFZ process can be very suitable to grow Bi-$n = 1$ single crystals. However, they investigated only the composition $Bi_{2.4}Sr_{1.6}CuO_{6+z}$ and unfortunately, their crystals were not superconducting. Crystal growth by TSFZ on other compositions have not been investigated so far.

In this paper we describe crystal growth of various compositions in the Bi-$n = 1$ system by means of the TSFZ method. Besides the nominal composition $Bi_2Sr_2CuO_{6+z}$ we studied the composition in the middle of the stability region of the R-phase, i.e. $Bi_{2.3}Sr_{1.7}CuO_{6+z}$. Furthermore we investigated the influence of partial La substitution in the R-phase on the crystal growth process and the superconducting properties of the crystals.

2. Experimental

Choice for parameters in the TSFZ experiments.
The TSFZ experiments are carried out with an

arc-image furnace. In this furnace the radiation of a Xenon lamp (Philips, type CSX2500) is focused by means of two elliptical mirrors into the point Z. At this point two vertical polycrystalline rods with the same composition as the intended crystal composition are brought close together, thereby creating a molten zone between the rods. The various TSFZ experiments have usually been accomplished with a given parameter sub-set which is summarized in table 1.

Although care has been taken to decrease the porosity of the polycrystalline rods, sometimes soaking problems occurred. In that case the density of the feed rod was further increased by premelting at a relatively high speed (about 80 mm/hr.). Subsequently, the premelted rod is used as feed rod in a slow pulling experiment.

Preparation and characterisation of the polycrystalline rods

The polycrystalline bars, used to grow single crystals of ceramic high-T_c superconductors with the TSFZ process, must meet three major requirements. The composition of the bars must be similar as the intended composition of the crystals to be grown, the porosity has to be low and the bars must be straight. Straight and dense ($p > 90\%$) single phase polycrystalline rods have been prepared by a conventional solid state reaction of a mixture of Bi_2O_3, $SrCO_3$, La_2O_3 and CuO powders to form the ceramic compound. Details about the preparation of the various compounds can be found elsewhere [13].

Table 1. Parameter subset for the TSFZ experiments.

composition feed comp. seed comp. solvent	crystal comp. idem self created
diameter feed (mm) diameter seed (mm) pulling rate (mm/h) rotation feed (rpm) rotation seed (rpm) density feed (%)	4-8 idem 0.8-4 +60 -60 ≥ 90
environment pressure (bar)	air 2

The materials have been characterized by X-ray powder diffraction, ac susceptibility measurements (χ_{ac}) and Electron Probe Micro-analysis (EPMA).

3. Results

$Bi_2Sr_2CuO_{6+z}$

The prepared polycrystalline rods ($p = 90\%$) consisted of the collapsed structure and were not superconducting. Several crystal growth experiments have been carried out with these bars and they all yielded boules with needle-like crystals, a crystal shape which is indicative for the semiconducting collapsed phase [14]. Powder X-ray diffraction patterns of the crushed needles indicated that both the R-phase and the collapsed phase are present, but nevertheless the as-grown crystals were not superconducting. Subjecting the as-grown crystals to annealing experiments at elevated temperatures ($>800\,^{\circ}C$), followed by quenching into liquid N_2 (LN$_2$), yielded $T_c = 9$ K. However, the χ_{ac} signal was very small, indicating the absence of bulk superconductivity.
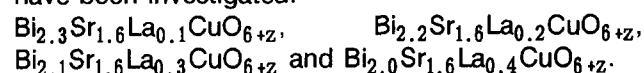
$Bi_{2.3}Sr_{1.7}CuO_{6+z}$

Polycrystalline bars with a nominal composition $Bi_{2.3}Sr_{1.7}CuO_{6+z}$ have been prepared according to the preparation route as reported by Sinclair et al. [8]. Powder X-ray diffraction showed that the rods consist of the R-phase. Nevertheless they do not show superconductivity, and attempts to introduce superconductivity by annealing experiments were unsuccessful. The TSFZ experiments with these polycrystalline bars yielded large plate-like crystals with lateral dimensions of 10 ×3 mm^2 and a thickness of about 0.1 mm. These crystals could be separated easily from the boules by mechanical cleavage. The plate-like morphology and the facility upon cleavage indicate that the crystals exhibit the R-phase [14]. This was confirmed by powder X-ray diffraction, because all the peaks in the diffraction pattern could be indexed within the R-structure. Furthermore, a Θ-2Θ scan with the incident Cu-Kα X-ray beam at an angle Θ with the crystal plate revealed that the crystal plate coincides with the crystallographic a,b-plane, and from the ($00l$) reflections we find c = 2.461 nm, in close agreement with other reports [8]. The composition of the platelets has been determined by EPMA and is given by $Bi_{2.3\pm0.03}Sr_{1.8\pm0.05}Cu_{0.9\pm0.1}O_{6+z}$ i.e. close to the intended composition.

The as-grown platelet crystals were not superconducting. We have attempted to introduce superconductivity by annealing experiments. These

experiments have been performed at different temperatures T_{ann} in air or pure O_2. The crystals are cooled by quenching into LN_2. With T_{ann} between 450 °C and 885 °C, it appeared not possible to obtain superconductivity. The absence of superconductivity might be due to over-doping with trivalent bismuth. The substitution of divalent strontium by Bi^{3+} decreases $pCuO_2$ so much that the superconducting region in the phase diagram can not be reached with changes in the oxygen content brought about by the annealing experiments.

$Bi_{2+x}Sr_{1.6}La_yCuO_{6+z}$ (x+y = 0.4)

In view of the positive crystal growth results of $Bi_{2.3}Sr_{1.7}CuO_{6+z}$, we studied the partial replacement of Sr by La into the solid solution Bi_{2+x}-$(Sr,La)_{2-x}CuO_{6+z}$. The following four compositions have been investigated:

$Bi_{2.3}Sr_{1.6}La_{0.1}CuO_{6+z}$, $Bi_{2.2}Sr_{1.6}La_{0.2}CuO_{6+z}$,
$Bi_{2.1}Sr_{1.6}La_{0.3}CuO_{6+z}$ and $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$.

The prepared polycrystalline rods (ρ > 95%) consist only of the R-phase and do not contain the collapsed phase. This indicates that the introduction of La into the solid solution $Bi_{2+x}(Sr,La)_{2-x}CuO_6$ stabilizes the formation of the R-phase. The superconducting onset temperature of the polycrystalline material has been determined by χ_{ac} experiments. The results of these experiments are summarized in table 2. Despite the presence of the R-phase in all compounds, only the two compounds with the highest La substitution show superconductivity above 4.2 K. This result indicates that $pCuO_2$ is not solely determined by the amount of trivalent cations in the composition. Indeed, two effects in addition to the cation valencies have been reported to determine $pCuO_2$. First of all, the introduction of La^{3+} for Sr^{2+} directly influences the amount of excess oxygen z in the Bi_2O_{2+z} layers. Partly, this effect is caused by the different ionic radii of Sr^{2+} and La^{3+}. For instance, in $Bi_2Sr_{2-x}La_xCuO_{6+z}$ it has been found [4] that z increases with increasing x, thereby compensating the decrease of free holes introduced by La^{3+}. Secondly, it has been noticed that the mobile holes do not necessarily contribute to $pCuO_2$ planes, but may partly be present in the Bi_2O_{2+z} layers [4].

After sintering, the polycrystalline compounds were either furnace cooled or quenched into LN_2. The influence of the cooling procedure on T_c is summarized in table 2. Apparently, the two superconducting compounds need oxidizing circumstances for an optimum T_c. For $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$ a maximum T_c of 28 K is found, in close agreement with other reports [4,5].

Table 2. Influence of the cooling procedure on T_c of polycrystalline rods with nominal compositions $Bi_{2+x}(Sr,La)_{2-x}CuO_{6+}$. The rods are either furnace cooled (f.c.)or quenched into LN_2.

compound composition	f.c.	LN$_2$
$Bi_{2.3}Sr_{1.6}La_{0.1}CuO_6$	ns	ns
$Bi_{2.2}Sr_{1.6}La_{0.2}CuO_6$	ns	ns
$Bi_{2.1}Sr_{1.6}La_{0.3}CuO_6$	16	15
$Bi_2Sr_{1.6}La_{0.4}CuO_6$	28	20

The polycrystalline bars were used as feed/seed rods in the TSFZ experiments. Again, the resulting boules could be cleaved along the growth direction and contained platelet crystals. The lateral dimensions of these platelets were typically 2×0.5 mm^2, significantly smaller than for the $Bi_{2.3}Sr_{1.7}$-CuO_{6+z} crystals. The thickness was about 0.1 mm. Powder X-ray diffraction on crushed crystals revealed only the R-phase, and a Θ-2Θ scan with the X-ray beam at an angle Θ with the plate direction revealed that the crystal plate coincides with the crystallographic a,b-plane. The T_c of the crystals increases with the nominal La content in the polycrystalline feed rod. The expected maximum value T_c = 27 K is achieved for $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$. Subsequently, we subjected such a $Bi_{2.0}Sr_{1.6}La_{0.4}$-CuO_{6+z} crystal to annealing treatments in order to improve T_c. Table 3 summarizes these results. Low oxygen contents correspond to low T_c-values, a tendency which is essentially similar as found for polycrystalline $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_6$; this means that apparently the introduction of La lowers $pCuO_2$ to such an extend that one arrives at the low concentration side of the dome shaped T_c-$pCuO_2$

Table 3. Influence of annealing experiments on T_c of $Bi_2Sr_{1.6}La_{0.4}CuO_{6+z}$ crystals.

T_{ann} (°C)	environ.	cooling proc.	T_c(K)
as grown	—	—	27
600	O$_2$	LN$_2$ quenched	28
800	O$_2$	T_{room} 15°C/hr	29
800	3% O$_2$	vac.quenched	25
800	0.3% O$_2$	vac.quenched	25

phase diagram [1].

The temperature dependence of χ_{ac} for an as-grown and an annealed $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$ crystal (T_{ann} = 800 °C/O_2, followed by slow cooling (15 °C/hr) to T_{room}) is shown in fig. 1. Besides a slight increase of T_c, the annealing procedure induces a much sharper transition. The decrease of the transition width indicates that the crystal exhibits a more homogeneous structure. After annealing, the transition width is ΔT_c = 7 K (10%-90% of the χ_{ac} signal).

4. Conclusions

In this paper we have shown that single crystals of the Bi-n = 1 system can be grown successfully by means of the TSFZ method. Except for the stoichiometric composition $Bi_2Sr_2CuO_{6+z}$, the TSFZ experiments on all the examined compositions yield plate-like crystals of the layered R-phase, which could be cleaved from the boules. The plates are thin with lateral dimensions of a few millimeters and a thickness of about 0.1 mm. The plate direction coincides with the crystallographic a,b-plane. The largest crystals have been obtained after zone melting of $Bi_{2.3}Sr_{1.7}CuO_{6+z}$. Crystals from this compound exhibit lateral dimensions of about 15×4 mm^2. However, these crystals are not superconducting, and attempts to introduce superconductivity by annealing were unsuccessful up till now.
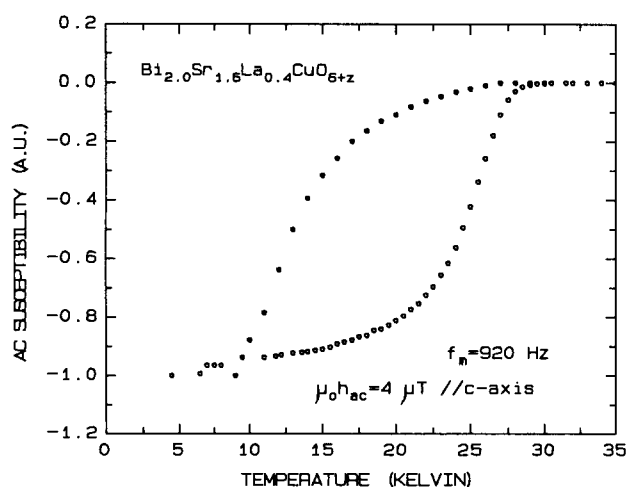
Superconducting crystals have been grown by substitution of divalent Sr by trivalent La in the solid solution $Bi_{2+x}(Sr,La)_{2-x}CuO_{6+z}$. The superconducting onset temperature of these crystals depends on the nominal La content in the feed rod. The highest T_c is obtained for crystals with nominal composition $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$. As-grown, these crystals exhibit superconductivity at 27 K. The superconducting transition is rather broad, but could be improved considerably by annealing (after annealing ΔT_c = 7 K). A drawback of the introduction of La into the feed material is that the crystals exhibit smaller lateral dimensions.

References

[1] M.R. Presland, J.L. Tallon, R.G. Buckley, R.S. Liu and N.E. Flower, Physica C176 (1991) 95.

[2] B.C. Chakoumakos, P.S. Ebey, B.C. Sales and E. Sonder, J. Mater. Res. 4 (1989) 767.

[3] P.V.P.S.S. Sastry, J.V. Yakhmi, R.M. Iyer, C.K. Subramanian and R. Srinivasan, Physica C178 (1991) 110.

[4] W.A. Groen, D.M. de Leeuw and G.M. Stollman, Solid State Commun. 72 (1989) 697.

[5] J. Darriet, C.J.P. Soethouy, B. Chevalier and J. Etourneau, Solid State Commun. 72 (1989) 697.

[6] E. Sonder, B.C. Chakoumakos and B.C. Sales, Phys. Rev. B40 (1989) 6872.

[7] Y. Ikeda, H. Ito, S. Shimomura, Y. Oue, K. Inaba, Z. Hiroi and M. Takano, Physica C159 (1989) 93.

[8] D.C. Sinclair, J.T.S. Irvine and A.R. West, Jpn. J. Appl. Phys. 29 (1990) L2002.

[9] S.A. Sunshine, L.F. Schneemeyer, R.M. Fleming, A.T. Fiory, S. Martin and S.H. Glarum, Mol. Cryst. Liq. Cryst. 184 (1990) 9.

[10] P. Strobel, B. Bonnet, C. Mouget and B. Souletie, Physica C172 (1990) 193.

[11] K. Remschnig, J.M. Tarascon, R. Ramesh and G.W. Hull, Physica C175 (1991) 261.

[12] M. Matsumoto, J. Shirafuji, K. Kitahama, S. Kawai, I. Shigaki and Y. Kawate, Physica C185-189 (1991) 2015

[13] J.H.P.M.Emmen, Ph. D. Thesis, Eindhoven University (1992) The Netherlands.

[14] P. Strobel, K. Kelleher, F. Holtzberg and T. Worthington, Physica C156 (1988) 434.

Figure 1. Superconducting transition of a $Bi_{2.0}Sr_{1.6}La_{0.4}CuO_{6+z}$ crystal, as grown and after annealing. The annealing experiment consisted of a heat treatment at 800 °C in O_2, followed by slow cooling (15 °C/hr.) to T_{room}.