Structural Properties of CaLaBaCu$_3$O$_{7-\delta}$ Single Crystals Grown by Self-Flux Method

L.T. Corredor[a], D.A. Landínez Téllez[a], Jairo Roa Rojas[a], and J. Albino Aguiar[b]

(a)Physics of Novel Materials Group, Department of Physics,

National University of Colombia, A.A. 14490, Bogotá, D.C., Colombia

(b) Laboratório de Supercondutividade e Materiais Avançados, Departamento de Física

Universidade Federal de Pernambuco, 50670-901, Recife, PE, Brasil

Millimeter-sized single crystals of CaLaBaCu$_3$O$_{7-\delta}$ were grown by the conventional self-flux technique. In this report we present a characterization of the structural and morphological properties of our first time grown single crystals. X-Ray diffraction patterns show that the unit cell of the samples corresponds to a tetragonal structure. SEM images evidence excellent morphological properties without presence of twins. EDX measurements show the difficulty of Ca to enter in the structure. The implications of our results are extensively presented and discussed.

1 Introduction

A major problem related to the understanding of the physical mechanisms involved in High T_c superconductivity, is the diversity of properties among different superconductor compounds and essentially, the need of having pure samples, to get information without the influence of the characteristic disorder of cuprate oxides. Because of that, growth of single crystals provides the best study tool to access the typical phenomenology of the High T_c superconductivity. In the systems RE:123 there is a compound not thoroughly explored, and in contrast with the superconductor Y:123, has a tetragonal structure. It is the CaLaBaCu$_3$O$_{7-\delta}$; [CLBCO] it has been considered to be derived from YBa$_2$Cu$_3$O$_{7-\delta}$ [YBCO] by replacement of Y by Ca and randomly, Ba by La.[1, 3] This distribution of Ca and La ions makes the oxygen sites O(4) and O(5) in the CuO chains randomly occupied, forming in that way, a tetragonal structure independent of the oxygen content. This compound is a triple perovskite structure compound, (a= 3.87 Åand c = 11.71 Å, space group P4/mmm) and isostructural with the tetragonal YBa$_2$Cu$_3$O$_{7-\delta}$.[4] In spite of their similarity, contrasting with the YBCO, the boundary between the superconducting and non superconducting phases of CaLaBaCu$_3$O$_{7-\delta}$, is defined only by oxygen content, without the complexity of the self-doping effects and the tetragonal- orthorhombic transition of crystalline structure, proper of the YBa$_2$Cu$_3$O$_{7-\delta}$. [5] Since the CaLaBaCu$_3$O$_{7-\delta}$ structure remains always tetragonal, independently of the oxygen content, the phase is congruent and the system does not present *twins* formation. [2] The study of single-crystalline samples of this compound has a great interest, since its properties are unusual contrary to the conventional superconducting oxides. Despite its critical temperature being slightly lower, in this system the anisotropy factor is considerably smaller, consequently, the critical transport current density is raised [6], which represents a greater possibility of technological application.

2 Crystal growth

The crystals were grown by using a self-flux method similar to that reported by Scneemeyer et. al..[7] A mixture was prepared from CaO (99.9%), La$_2$O$_3$ (99.98%), BaO (99.9%) and CuO (99%) powders with molar ratios 1:2:2:12, 1:2:2:10 and 0.5:1.5:3:12, as shown in table 1. Some authors have studied the Ca$_x$La$_{1.5-y}$Ba$_{1.5-x+y}$Cu$_3$O$_z$ family, and suggested that perhaps the 1113 phase could be not a single phase.[5, 6, 9, 10] Consequently, there is no consensus of opinion on the stoichiometry ranges of single phase samples. According to those authors, the critical temperature reaches a maximum of 78 K in the composition Ca$_{0.5}$LaBa$_{1.5}$Cu$_3$O$_{7-\delta}$, not in the 1113 phase as we thought. Then we made three batches with this starting stoichiometry. The ratios were considered based on the molar ratios used in the growth of YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals, since their structural properties are similar.[8] The mixture was placed on different crucibles depending on the batch. One of them was made of alumina covered with Au that is widely used because it is cheaper and does not contaminate the samples. The crucible with the mixture was heated up to 300° in 30 min. and during 2 hours. Then it was heated to 1100° at a rate of 1.3°/min and kept at this temperature for 4 hours. The following step was a slow cooling to room temperature at a rate

of 0.6°/min. The as-grown crystals have often low and inhomogeneous oxygen content. Then, they were annealed in O_2 atmosphere at 450° for 7 days. The crystals were placed on a polycristalline CLBCO pellet, inside a quartz tube. Crystals produced in this way had typical dimensions of 0.4×0.4 mm^2 in the **ab** plane, and 0.02 mm along the **c** direction. Although crystals with larger area were occasionally obtained, their extraction from the flux was very difficult.

Table 1. Stoichiometries and crucibles used

Phase wished	Sample	Initial stoichiometry	Crucible
$CaLaBaCu_3O_{7-\delta}$	C1	$CaLa_2Ba_2Cu_{12}O_{7-x}$	ZrO_2
	C2	$CaLa_2Ba_2Cu_{10}O_{7-x}$	Al_2O_3
$Ca_{0.5}LaBa_{1.5}Cu_3O_{7-x}$	C3	$Ca_{0.5}La_{1.5}Ba_3Cu_{12}O_{7-x}$	Al_2O_3
	C4	$Ca_{0.5}La_{1.5}Ba_3Cu_{12}O_{7-x}$	Al_2O_3
	C5	$Ca_{0.5}La_{1.5}Ba_3Cu_{12}O_{7-x}$	Platinum

3 Characterization

3.1 Experimental

The morphological properties of the obtained crystals, were initially examined by metallographical microscopy of light reflection and scanning electron microscopy (SEM), obtaining the images on Fig. 1. The oxygenated crystals were examined with energy dispersive X-Ray analysis (EDX) to find out about the correct composition and the presence of second phases. Some were analyzed by X-Ray diffraction technique. The diffraction patterns were collected by a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (1.5406 Å) at room temperature, and taken from 2Θ =10° to 70°. Diffraction data were analyzed by the *Carine* software for spectrum analysis.
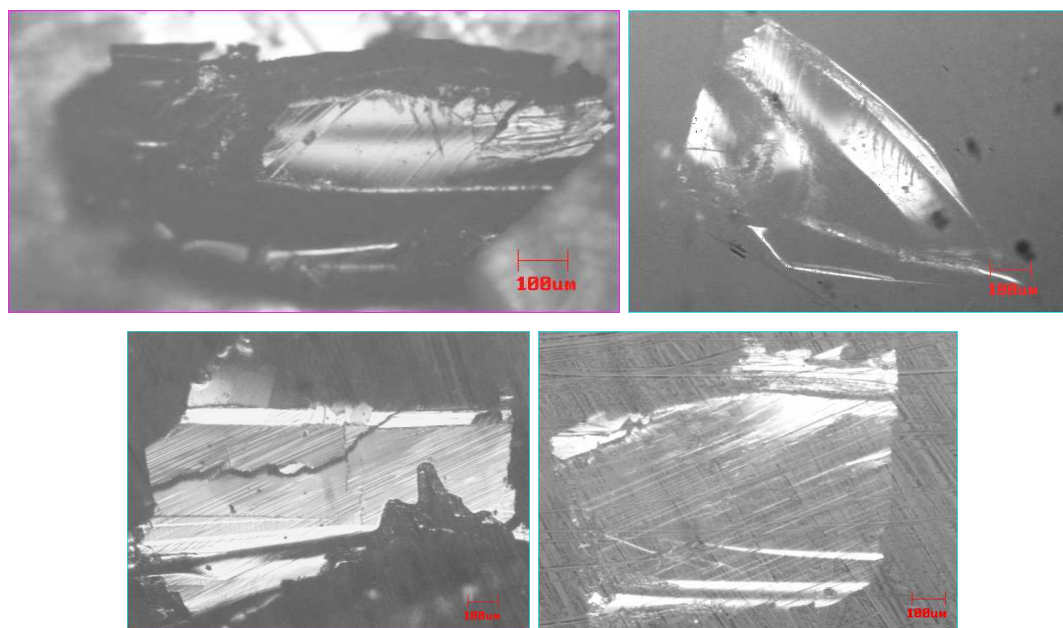

Figure 1. Metallographical and SEM microscopy images: (a) C1-1, single crystal from C1 batch. (b) C2-1. (c) C3-1. (d) C5-1, from up left clockwise.

4 Results and discussion

In the batches C1 and C2 we did not get single crystals with adequate morphological properties, i.e., they presented irregular surfaces. Nevertheless, some elongated shaped crystals, which we called "needles", grew together with the others (see Fig. 2). These crystals did not have twins, hopefuly due to the tetragonal nature of the compound. The batches C3, C4, and C5 provided better crystals, although little sized, approximately 0.4mm x 0.4mm (Fig.1c-d). Needles showed up always in all batches, with average size 0.3mm x 3mm. In the last batch we observed some lines like

twins in the surface of the square shaped crystals (Fig.1d), but posterior characterizations showed their true origin.

With the X-Ray diffraction patterns, intensity and position profiles were fitted to the theoretical pattern of the structural model of the tetragonal form of the Y-123 compound, which belongs to space group P4/mmm, i.e. replacing Yttrium by Calcium and one Lanthanum in one Barium site. This pattern belongs to the polycristalline compound, since there are not reports about CLBCO single crystals. We compared the positions and intensities of both patterns, only for the peaks involved in the single crystal one. These are shown in Fig. 3. This figure shows two main peaks in the experimental pattern: (110) and (220), which evidence the oriented growth of the sample. It becomes evident, from this figure, that the coincidence is total with the analogue peaks in the polycristalline pattern, both in position and intensity relation, besides of coinciding with other reports about the polycristalline compound.[9, 11, 12] It appears to be quite interesting that the single crystal grew in a different orientation of the expected one, i.e., with the *c* axis perpendicular to the crystal's surface, like YBCO single crystals.[13, 14] This is the explanation for the lines on the single crystal's surface, corresponding to oriented planes, not to twins. By means of pattern fitting, we obtained the cell parameter *c* as c = 11.71(4) Å, with a = b = 3.87(7) Å; these results agree with previous reports.[15]
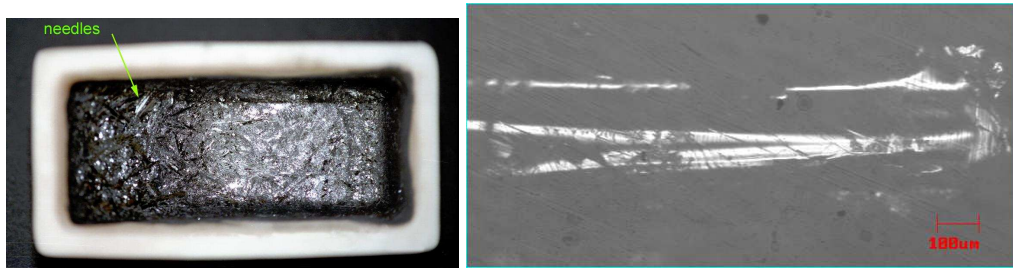

Figure 2. (a) Alumina crucible with needle-shaped single crystals no extracted (b) needle extracted from batch C4.
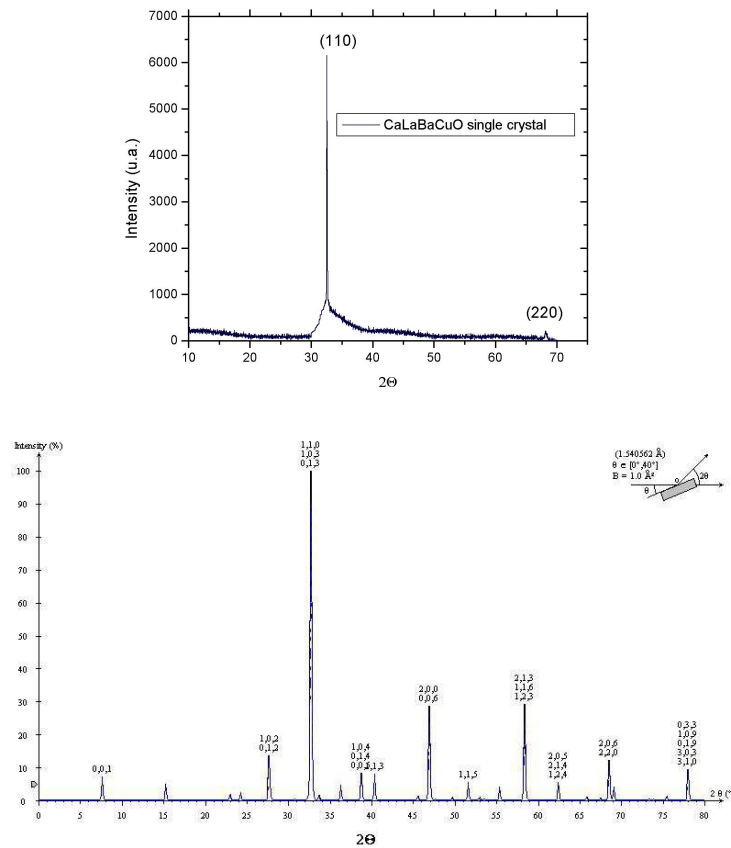

Figure 3. Experimental pattern (single crystal) and theoretical pattern (polycristalline).
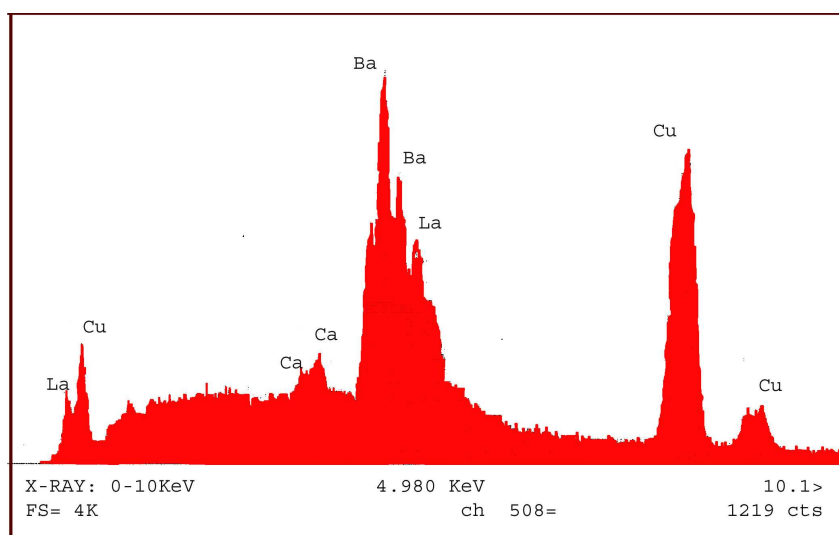
Figure 4. EDX analysis for C4-1 CaLaBaCuO single crystal.

The EDX analysis (Fig. 4) shows the proper peaks and gives an indication of the pure-phase character of the sample. This analysis revealed that in all the batches there were second phases present, like CuO, corresponding to the *needles* discussed above. LaBaCuO crystals were often obtained too; all the batches revealed a possible difficulty in the entrance of calcium into the structure. On this regard, there are reports from Y:123 doped with calcium, in which the calcium enters into the phase-pure structure only up to 15%.[16] After this limit, other phases begin to appear. In brief, although it is found that the calcium introduction improves the carrier density, and therefore the superconductor properties, the calcium's entry is not always reached .[17]This is due to the reduced ionic radio of calcium (2.23 Å), that although is similar to the yttrium's (2.27 Å), is reduced compared with the lanthanum's (2,.74 Å) and barium's (2.78 Å); these occupy randomly the same sites as calcium. Consequently, the solid solubility is limited. Nevertheless, it is noticeable the absence of Al and Au in samples from C2, C3 and C4. In the case of C5, we obtained samples with the adequate properties, besides of no contamination, except for the crystals removed from the walls. Further investigation of these crystals are under way, aimed to verify their superconductor character.

Acknowledgements

References

[1] Y. Yokura, J.B. Torrance, T.C. Huang, and A.I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[2] D.M. de Leeuw. C.A.H.A. Mutsaers, H.A.M. van Hal, H. Ver-wij, A.H. Carim, and H.C.A. Smoorenburg, Physica C **156**, 126 (1988).

[3] T. Bjornholm, I.K. Schuller, E.A. Early, M.B. Maple, B. Wuyts, J. Vanacken, and Y. Bruynseraede, Phys. Rev. B. **41**, 11154 (1990).

[4] R.A. Gunasekaran, J.V. Yakhmi, and R.M. Iyer, Physica C **208**, 143 (1993).

[5] K. Yamaya, T. Yagi, and Y. Okajima, Solid State Comm. **87**, 1113 (1993).

[6] J.L. Peng, P. Klavins, R.N. Shelton, and H.B. Radousky et al., Phys. Rev. B. **39**, 9074 (1989).

[7] L.F. Schneemeyer, J.V. Waszcak, and T. Siegrist et al., Nature **328**, 601 (1987).

[8] E.F. Righi, S.A. Grigera, G. Nieva, and F. De la Cruz, Superconductivity Review **2**, 205 (1998).

[9] J.M.S. Skakle and A.R. West, Physica C **220**, 187 (1994).

[10] T. Mertelj, P. Stastny, F.C. Matacotta, P. Ganguly, and C.U. Segre, Physica C **183**, 11 (1990).

[11] V.P.S Awana and A.V. Narlikar, Mod. Phys. Lett B **15**, 415 (2001) 415.

[12] Y. Sato., M. Valkeapää, V. Petrykin, M. Osada, H. Rundlöf, S. Eriksson, and M. Kakihana, NFK Experimental Report No.549 (2002).

[13] S.N. Barilo, A.P. Ges, S.A. Guretskii, D.I. Zhigunov, A.V. Zubets, A.A. Ignatenko,A.N. Igumenster, I.D. Lomako, A.M. Luginets, V.N. Yakimovich, and L.A. Kurochkin, J. Crystal Growth **119**, 403 (1992).

[14] J.P. Rice and D.M. Ginsberg, J. Crystal Growth **109**, 432 (1991).

[15] J.M.S. Skakle and A.R. West, Physica C **241**, 191 (1995).

[16] V.P.S. Awana, A. Tulapurkar, S.K. Malik, and A.V. Narlikar, Phys. Rev. B **50**, 549 (1994).

[17] S.K. Malik, W.B. Yelon, and V.P.S. Awana Mod. Phys. Lett. **10**, 845 (1996).