JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 919 - 922

T_c behaviour of 2212 and 2223 phases in $(Bi,Pb)Sr(Ca_{2-x}Y_x)CuO/2223$

V. MIHALACHE*, G. ALDICA
National Institute of Materials Physics, Bucharest-Magurele, POB MG-7, 077125, Romania

The critical temperature, T_c, for $(Bi,Pb)Sr(Ca_{2-x},Y_x)CuO/2223$, with x between 0 and 0.45, polycrystalline samples have been investigated. T_c of $(Bi,Pb)_2Sr_2Ca_{2-x}Y_xCu_3O_{10+\delta}$ phase, 2223, found in samples with $x<0.05$, decreases whereas T_c of $(Bi,Pb)_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ phase, 2212, found in samples with $x>0.05$, displays a parabolic dependence with the increase of Y content. The change of T_c for 2223 originates mainly from the increase of x. The variation of both x and oxygen content, δ, influences the T_c of 2212. The *doping* state of 2212 and 2223 in Y substituted samples suggests that, generally, in the samples consisting of both superconducting phases, 2212 is in *over-doped* state whereas 2223 is in *under-doped* state. The last affirmation suggests that 2212 could bring a significant contribution in the transport parameters of (Bi,Pb)SrCaCuO/2223 samples.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: 2223, 2212, Y substitution, Critical temperature, Doping state

1. Introduction

One of the important factors which influences the superconducting parameters of (Bi,Pb)SrCaCuO/2223, the material with the higher potential for applications, is the presence of 2212. Obvious correlation between the superconducting parameters (i.e. critical current density) and the ratio of 2212 could not be yet established. An example is that the inclusion of 2212 in the 2223 matrix may act as a weak link as well as a pinning site and this depends on the 2212 volume fraction, its morphology [1-3], etc. Therefore, it is useful to study separately the behaviour of 2212 and 2223, both of them being comprised in the same (Bi,Pb)SrCaCuO/2223 pellet. A method which makes possible such a study is the *ac* susceptibility measurement.

The marked effect on the superconducting properties of both 2212 and 2223 has the oxygen stoichiometry. This can be controlled by varying the treatment conditions - oxygen partial pressure and the annealing temperature [4]. Another modality of changing the oxygen stoechiometry is the extra-element doping into the nominal formula.

In this paper we study the T_c behaviour of yttrium doped 2212 and 2223 by *ac* susceptibility measurements. T_c of the doped samples proved to be influenced by variation of x as well as by changing the oxygen content. Unlike to data reported in literature, the 2212 phase was obtained by using the nominal composition and the treatment conditions specific for 2223; moreover, for x between 0.05 and 0.11 both studied superconducting phases were comprised in the same pellet.

2. Experimental

The samples were prepared by the conventional solid-state reaction method. $SrCO_3$, $CaCO_3$, Y_2O_3 and CuO powders were mixed in the molar ratio Sr:Ca:Y:Cu = 2:2-x:x:3 (with x between 0 and 0.45) and pressed into 9×12×3 mm^3 pellets at 0.083 GPa. The pellets were calcinated with three intermediate grindings at temperatures between 924 °C -950 °C for 85 hours, reground then Bi_2O_3 and PbO powders were added to obtain the following ratio between components Bi:Pb:Sr:Ca:Y:Cu - 1.8:0.4:2:2-x:x:3. The powders were pressed into 3×3×10 mm^3 pellets at 0.75 GPa and calcinated at 815 °C for 20 hours in air, reground and pressed again into 3×3×10 mm^3 pellets at 0.75 GPa. Finally, the sintering thermal treatment was performed in air at 855°C for 330 h (with an intermediate grinding) for samples of set Y1, and at 850°C for 500 h (with an intermediate grinding) for samples of set Y2. All samples belonging to a set were treated simultaneously in the same crucible. Moreover, during the thermal treatment the samples were imersed in the powder of nominal composition $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$.

X-ray diffraction (XRD) measurements were performed using the CuK_α radiation. Zero field cooled (ZFC) *ac* susceptibility measurements were performed using Oxford Instruments cryostat of MagLab 2000 System at H_{ac}=3 Oe, H_{dc} =0.01T and frequency ν = 1000Hz. Also, the measurements at H_{ac} = 0.063 Oe, H_{dc} = 0 and frequency ν = 5500 Hz were performed.

To distinguish between the doping with Y and the *doping* state determined by the total number of holes in CuO_2 plains we shall describe the first situation by normal fonts (i.e. doped) and the second one by italic fonts (i.e. *doped*).

3. Results and discussion

The volume fraction, *f*, of the 2212 and 2223 phases of the samples from set Y2 were estimated from XRD patern as $f^{2212}=\dfrac{A(008)_{2212}}{A(008)_{2212}+A(0010)_{2223}}$ and $f^{2223}=\dfrac{A(0010)_{2223}}{A(0010)_{2223}+A(008)_{2212}}$, respectively, where $A(0010)_{2223}$ and $A(008)_{2212}$ represent the peak area for the reflections $(0010)_{2223}$ and $(008)_{2212}$, respectively. The details of XRD measurements and the estimation of *f* values for both sets will be reported elsewhere. f^{2223} decrea whereas f^{2212} increases with increasing *x*. The non-doped sample contains only 2223, the sample with x=0.05 has 45% of 2223 and the samples with $x \geq 0.10$ have only 2212.

The ratio of superconducting phases for samples of set Y1 was estimated from $\chi'(T)$ curves of *ac* susceptibility measurements. Again, the non-doped sample contains only 2223, the sample with x=0.05 has 40% of 2223 and the samples with $x \geq 0.11$ have only 2212.

In Fig.1 is given the $c(x)$ dependence for 2223 and 2212 of samples from set Y2 estimated from XRD patterns.

The *c*-axis length of 2212 decreases with increasing *x* in agreement with literature (see ref . [5]). The $c(x)$ of 2223 behaves in the same manner as that of 2212. One of the reasons of c-axis decreasing for 2212 is suggested to be the increasing internal pressure due to bigger Y ionic radius in respect to Ca ionic radius [6]. The important contribution in change of *c* axis length have the variation in oxygen stoichiometry ([7] and references therein). This is valid for our samples too, as will be shown below.

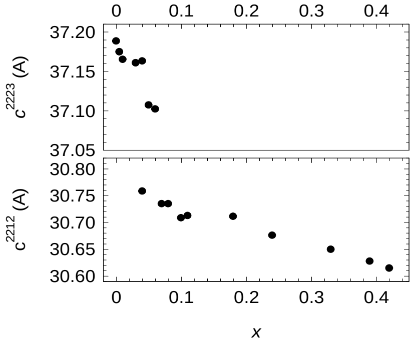

Fig. 1 The c-axis length dependence on x for 2223 and 2212.

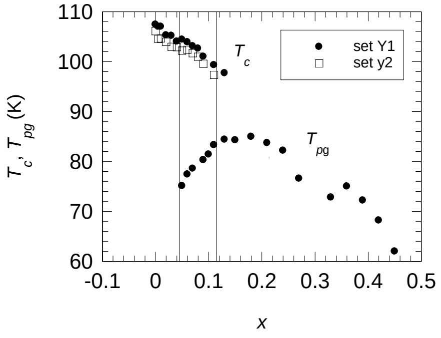

Fig. 2 $T_c(x)$ dependence (determined from $\chi'(T)$ curves) for 2223 and $T_{pg}(x)$ dependence (estimated from $\chi''(T)$ curves) for 2212.

The *ac* susceptibility curves of our single-phase samples display the typical behaviour as the polycrystalline samples: two steps in χ'(T), one at higher temperatures corresponding to diamagnetic signal of the grains and another at lower temperature corresponding to diamagnetic shielding of the sample through the weak links between the grains; two peaks in χ''(T), one situated at higher temperature attributed to the losses in the grains (T_{pg}) and another situated at lower temperature attributed to the losses in the inter-granular network (T_{pj}). At the certain value of the temperature, T_{pg} and T_{pj}, the full penetration of the field into the grains and into the sample through weak links, respectively, occurs.

T_c values for 2223 were determined from the onset of $\chi'(T)$ curves measured at H_{ac} = 0.063 A/m, H_{dc}=0 and ν = 5500 Hz. The conditions of measurements like this, namely the small fields , could not be used for T_c of 2212 estimation from $\chi'(T)$ with desired accuracy; the main hindrance is the signal coresponding to weak-links network which, can overlap the intra-granular signal. However, the relatively small *dc* fields superimposed on *ac* one shifted the inter-granular signal at temperautures values lower than 2212 intra-granular signals in single 2212-phase samples as well as in samples consisted of both 2212 and 2223 superconducting phases. Even in these conditions the T_{pg} peak position of 2212 can be estimated with higher precision than the onset temperature T_c of 2212 in the samples containing also 2223. This is the reason we have operated with T_{pg} values instead T_c of 2212. T_{pg} values for 2212 grains were estimated from χ''(T) curves measured at H_{ac} = 3 Oe, H_{dc} = 0.01 T and ν = 1000 Hz.

In Fig. 2 are shown the $T_c(x)$ and $T_{pg}(x)$ dependences for 2223 and 2212, respectively. It can be seen that T_c of 2223 decreses whereas T_{pg} of 2212 displays a parabola, with a maximum at $x \approx 0.17$, with increasing of Y content.

T_{pg} of 2212 can be considered, with some aproximation, as T_c. This because $T_c(x)$ determined from both $R(T)$ and χ'(T) measurements (not shown here) behaves in very similar way as $T_{pg}(x)$ given in Fig 2. The arguments of the advantage of T_{pg} measurement were already given. The difference between T_c(x) and $T_{pg}(x)$ curves is not too big since the last was measured at relatively low fields compared to the first one. Moreover, in this paper the precision of absolute value of T_c is not so important, as the behaviour of this parameter with variation of Y content. Therefore, in the following we shall comment upon the T_c of 2212, being aware of that T_{pg} was measured.

The parabolic variation of T_c with the carrier-hole concentration, *p*, expressed as number of holes per Cu in CuO_2 planes, was first demonstrated for $La_{2-x}Sr_xCuO_4$ and appears to be a general feature in the phase diagram of HTC. The phase diagram was described by universal empiric relation given by S. D. Obertelli et al. [8]:

$$T_c/T_c^{\max} = 1\text{-}82.6(p\text{-}0.16)^2 \qquad (1)$$

As reported in literature, the average Cu valence of La and Y doped Bi-based oxides, determined by iodometric titration method [5], changes with increasing La and Y content, namely decreases. This suggests the parabolic variation of T_c with Y content, x, as well. Therefore, form Fig 2, it is obvious that the 2212 is optimal *doped* for $x \approx 0.17$, *over-doped* for $x<0.17$ and *under-doped* for $x>0.17$. As regarding 2223, the entire $T_c(x)$ curve lies in the *under-doped* region and, with some approximation, we can consider that this phase, for the sample without Y ($x=0$), is *optimal doped* (in reality it is slightly *under-doped*).

If we simply assume that Pb is divalent, Bi is trivalent, denote the average valence of Cu as $2+p$ and the oxygen content $10+\delta$ and $8+\delta$ for 2223 and 2212, respectively, then, p can be represented as:

$$p=2\delta/3-0.2/3-x/3 \quad \text{for 2223} \qquad (2.1)$$

$$p=\delta-0.1-x/2 \quad \text{for 2212} \qquad (2.2)$$

Supposing that optimal p is 0.16 at temperature $T_c^{\max,}$ we can estimate δ value for $x=0$ and $x=0.17$ for 2223 and 2212, respectively. Within the framework of set Y1 we obtained for non-doped 2223 $\delta=0.34$ and for 2212 with $x=0.17$ $\delta=0.345$.

Assuming that the oxygen content remains fixed at 0.34 and 0.345 for 2223 and 2212, respectively, the *doped* hole concentration, p, can be calculated across the substitution range ($x=0$-0.45) using equations (2.1) and (2.2). The resulted hole concentration is shown on the top scale of Figs. 3 and 4 for 2223 and 2212, respectively. In the same figures are shown the expected (dashed) curves based on universal equation (1). It can be seen that the obtained two $T_c(p)$ parabolic dependencies (one from our experiments and the other based on the universal equation) almost agree for 2223 (Fig. 3). Whereas for *under-doped* 2212, Tc of our samples does not fall as rapidly as expected (Fig.4). This discrepancy should be ascribed to the change of δ, namely the incorporation of additional oxygen into double Bi_2O_2 layer, for large values of x. This suggestion is in good agreement with already discussed decreases of c-axis length with increasing x. Indeed, A. Maeda et. al. [5] observed, using iodometric titration method, that the change in the average valence of Cu is much less than expected if assuming that δ does not change; they suggested that the origin of this discrepancy is the change of δ by changing the concentration of the substituting cations. It was suggested ([9] and references therein) that when Y(III) is introduced into the lattice it occupies the Ca(II) site, and due to its higher charge extra oxygen is also introduced into the Bi_2O_2 planes. At low Y substitution the intercalation of additional oxygen does not occur because the lattice is too dense. The later affirmation is valid for our 2223 and the *over-doped* Bi-2212 Therefore, the discrepancy of two parabolas shown in Fig.4 demonstrates the change of δ with increasing x. The increasing oxygen content was observed on HTS doped with La [10] and Y [11] by thermogravimetric method.

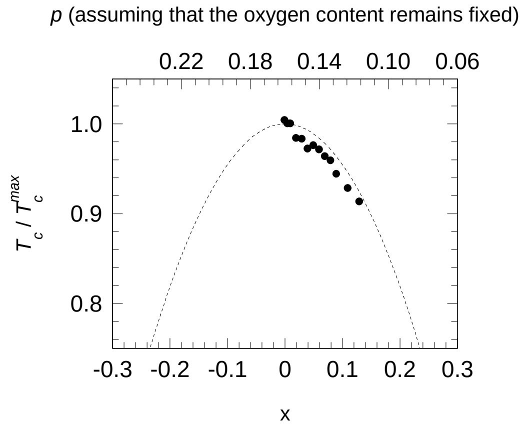

Fig. 3 The resulted hole concentration, p, from our experiments and the expected (dashed) curves based on universal equation (1) for 2223.

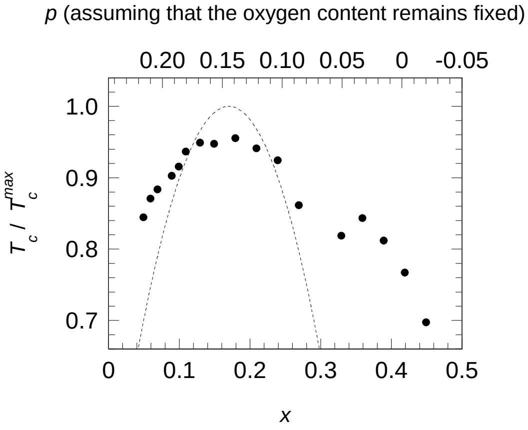

Fig. 4 The resulted hole concentration, p, from our experiments and the expected (dashed) curves based on universal equation (1) for 2212.

According to XRD results the panel of Fig. 2 can be divided in three regions of the phase compositions delimited by two vertical lines shown in the figure. The first region ($x<0.05$) comprises the samples with the majority 2223, the second region ($0.05<x<0.11$) the samples consisting of both 2223 and 2212, and the third region ($x>0.11$) the samples consisting of only 2212.

As we already emphasized, in the samples containing both superconducting phases (second region with $x=0.05$-0.11), the 2212 is *over-doped* whereas the 2223 is *under-doped*. In the following we argue that this is due to the different oxidation state of CuO_2 layers of these two superconducting phases.

One of the parameters, which describe the number of holes in HTS, in particular in Bi-based superconductors, is the thermopower. The values of the Seebeck coefficient, α, depend strongly on the condition of treatment due to change of oxidation states of the superconducting CuO_2 layers. An example is that the annealing in oxygen flux decreases the coefficient, α, since after oxygen annealing the specimens become more *doped*.

From Fig. 2 is clearly seen that in the same treatment conditions the 2223 of non-doped sample (x=0) presents a nearly optimal T_c, whereas T_c of non-doped 2212, which can be estimated by imaginary extrapolation of $T_c(x)$ curve to x=0, is situated in the *over-doped* region. This is in agreement with the literature, namely for similar treatment conditions the 2212 samples tends to be more doped than the 2223 samples ([7] and references therein). The disagreement with literature is that in our case both these superconducting phases are comprised in the same sample.

Our experience on hundreds samples showed that the Seebeck coefficient (which describes the number of holes), α, tends to be smaller, even negative, for as-grown samples with a large amount of 2212, whereas for the as-grown nearly single 2223 specimens it always have higher, positive, value. This is in good agreement with the *doping* state of 2212 and 2223 in Y doped samples when both these phases are comprised in the same sample ($0.05<x<0.11$). Therefore, it can be stated that, generally, in the non-doped (Bi,Pb)SrCaCuO2223 samples (x=0), consisted of both superconducting phases, 2212 is in *over-doped* state whereas 2223 is in *under-doped* state. This stresses the importance of 2212 in the value of Seebeck coefficient. In other words this superconducting phase may give a significant contribution in the transport parameters of (Bi,Pb)SrCaCuO/2223 samples.

4. Conclusions

We have studied the $T_c(x)$, x= (0 - 0.45), behaviour of 2212 and 2223 by *ac* susceptibility measurements. In addition to the data reported in literature, these two phases were studied when both of them are comprised in the same pellet. It was found that T_c of 2223 decreases whereas T_c of 2212 displays a parabolic dependence, with a maximum for $x \approx 0.17$, with increasing Y content. The change of T_c from 2223 originates mainly form the increase of x. However, for 2212, it proved to be influenced by variation of x as well as by changing of oxygen content, δ. We demonstrate that, generally, in the non-doped samples (x=0) consisted of both superconducting phases, 2212 is in *over-doped* state whereas 2223 phase is in *under-doped* state. This emphasizes that 2212 could has an important influence on the transport parameters of (Bi,Pb)SrCaCuO/2223 samples.

Acknowledgments

We thank the group of Laboratory of Physics, especially I. Deac, of the Babes-Bolyai University of Cluj-Napoca for their technical assistance. Also, we are grateful to the late I. Bradea for Seebeck coefficient measurements. The Ministry of Education and Research supported this work within the framework of the CERES program.

References

[1] S. X. Dou, H. K. Liu, Supercond. Sci. Technology **6**, 297 (1993).
[2] S. X. Dou, H. K. Liu, Y. C. Guo, Physica C **194**, p. 343 (1992)
[3] Y. C. Guo, H. K. Liu, S. X. Dou, Appl. Supercond. **1**, 25 (1993)
[4] R. G. Buckley, J. L. Tallon, I. W .M. Brown, M. R. Presland, N. E. Flower, P. W. Gilberd, M. Bowden, N. B. Milestone, Physica C **156**, 629 (1988).
[5] A. Maeda, M. Hase, I. Ysukada, K. Noda, S. Takebayashi, K. Uchinokura, Phys. Rev. B **41,** 6418 (1990).
[6] M. Kakihana, M. Osada, M. Kall, L. Borjesson, H. Mazaki, H. Yasuoka, M. Yashima, M. Yoshimura, Phys. Rev. B **53**, p. 11796 (1996).
[7] M. R. Presland, J. L. Tallon, R. G. Buckley, R. S. Liu, N. E. Flower, Physica C **176**, 95 (1991).
[8] S. D. Obertelli, J. R. Cooper, J. L. Tallon, Phys. Rev. B **46**, 14928 (1992).
[9] C. S. Gopinath, S. Subramanian, P. Sumana Prabhu, M. S. Ramachandra Rao, G. V. Subba Rao, Physica C **218**, 117 (1993).
[10] A. Maeda, M. Hase, I. Ysukada, K. Noda, S. Takebayashi, K. Uchinokura, Phys. Rev. B **41**, p. 6418 (1990)
[11] T. Kijima, J. Tanaka, Y. Bando, Jpn. J. Appl. Phys. **27**, p. L1035 (1988).

---

[*] Corresponding author: vmihal@infim.ro