JOURNAL OF SOLID STATE CHEMISTRY **108**, 164–169 (1994)

Yttrium Substitution for Calcium in $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$: Preparation and Study of Superconducting Phases

B. Himmerich,* H. Sabrowsky,* D.-N. Peligrad,†,[1] and M. Rosenberg†

*AG Festkörperchemie, Ruhr-Universität Bochum, Postfach 10 21 48, 4630 Bochum, Germany; and †Institut für Experimentalphysik VI, Ruhr-Universität Bochum, Postfach 10 21 48, 4630 Bochum, Germany

Received August 21, 1992; in revised form April 26, 1993; accepted May 7, 1993

Starting from the nominal compositions $Tl_2Ba_2Ca_{2-x}Y_xCu_3O_{10+\delta}$ after heat treatments in Ar atmosphere in gold sealed tubes, both superconducting phases "2223" and "2212" and the paramagnetic phase $BaCuO_2$ were present for zero and low Y concentration ($0 \leq x \leq 0.3$). The decrease of the critical temperature from 126 to 118 K for the 2223 phase and from 114 to 100 K for the 2212 phase was considered as evidence for Y substitution on Ca sites for low x values and corresponding reduction of the hole concentration per Cu atom. Higher Y concentrations ($x \geq 0.3$) destabilize the supercondncting phases. © 1994 Academic Press, Inc.

1. INTRODUCTION

The origin and concentration of the charge carriers in the high T_c superconductors $Bi_2Sr_2Ca_{m-1}Cu_mO_{2m+4}$ and $Tl_2Ba_2Ca_{m-1}Cu_mO_{2m+4}$ is still a controversial item. The hole-type conductivity in the normal state of these compounds and the superconductivity below a critical temperature T_c can be understood in terms of systematic deviations from the ideal stoichiometry, as a small excess of oxygen, for instance. In such a case the Tl-containing compounds with $m = 2$ (2212) and 3 (2223) have to be written as $Tl_2Ba_2CaCu_2O_{8+\delta}$ and $Tl_2Ba_2Ca_2Cu_3O_{10+\delta'}$, where δ and δ' represent the extra oxygen arising during the preparation procedure. It is usual to take for the hole concentration per Cu atom the values δ and $(2/3)\delta'$ for 2212 and 2223, respectively. The oxygen nonstoichiometry and therefore the hole density per Cu atom in the CuO_2 layers, respectively the average Cu valence, has a decisive influence on the transition temperature. Values for an optimal hole concentration at which T_c reaches a maximum were given in (3, 6–8, 22–26).

There are at least two ways to influence the hole concentration in order to study the correlation with the critical temperature T_c. The first one consists in changing the oxygen stoichiometry as was the case with Bi-2212, for instance, in (1). The second way is to perform suitable substitutions with ions with stable valencies 3+ or 2+ for Ca^{2+} or Bi^{3+}/Tl^{3+}, respectively. In the case of Bi-2212 the Ca ions can be completely substituted by lanthanide ions, as was shown in many studies (1–8). An interesting point is that in this case starting from the compositions $Bi_2Sr_2Ca_{1-x}Ln_xCu_2O_{8+\delta}$ for substitutions in the range $0 \leq x \leq 0.3$ practically no change in T_c besides sometimes a slight increase for very low x values occurred (2, 3, 5–8). For higher x values T_c started to decrease dramatically and the superconductivity was suppressed for $0.5 \leq x \leq 0.75$. An advantage for studying substitutions in Bi-2212 is the relatively high stability of this compound which permitted us to prepare single phases with the stoichiometric proportions of all the components others than oxygen and therefore to allow a reliable estimation of the oxygen off-stoichiometry δ and consequently the determination of the number of holes usually normalized per Cu atom. Such determinations imply obviously the stability of the valence state of all the ions other than Cu, a condition which in the case of Bi remains slightly questionable. The main result of these studies is the finding that a kind of quasiuniversal correlation between T_c and n_h can be considered as established in (6, 7). Relatively few similar studies were performed in the case of the Tl-containing high T_c superconductors (23–26). The main reason is the difficulty in preparing stoichiometric compounds of this type.

In the present paper we deal with the preparation and superconducting properties of the Y-substituted Tl-2223 compounds with nominal compositions $Tl_2Ba_2Ca_{2-x}Y_xCu_3O_{10+\delta}$. Expectations on an analogy with earlier results on Y substitutions in Bi-2223 could not be drawn because up to now, to our knowledge, in variance with the case of Bi-2212, no attempt to prepare $Bi_2Sr_2Ca_{2-x}Y_xCu_3O_{10+\delta}$ compounds was successful.

2. PREPARATION

The samples have been prepared in a closed system (9). The stoichiometric starting compositions $Tl_2Ba_2Ca_{2-x}$

---

[1] On leave from the Institute of Physics and Technology of Materials, P.O. Box MG-6, Bucharest, Romania.

0022-4596/94 $6.00

$Y_xCu_3O_{10+\delta}$ used for the preparation were obtained by mixing equimolar Tl_2O_3, CaO, Y_2O_3, and $BaCuO_2$ oxides in the corresponding proportions. In order to obtain $BaCuO_2$ equimolar mixtures BaO and CuO were grinded in an agate mortar and sintered at 1200 K in air for 24 h. All the starting oxides were then thoroughly powdered and ground in the agate mortar. The reaction took place in sealed gold tubes, which were placed into the outer, argon-filled, SiO_2 sealed tubes. The powders were heated in an Ar atmosphere in several steps: for 24 h at 713 K, for 12 h at 1123 K, and for 15 min at 1193 K.

In the first heating step, Tl_2O_3 decomposes into $Tl_2O_{3-\delta}$ according to the reaction (11, 12)

$$Tl_2O_3\,(s) \xrightarrow[24\,h]{713\,K} Tl_2O_{3-\delta}\,(s) + (\delta/2)O_2\,(g).$$

The decomposition of Tl_2O_3 prevents the formation of Cu_2O because the oxygen partial pressure stabilizes CuO. The argon (inert gas) atmosphere is necessary in order to inhibit the formation of $BaCuO_2$ and Ca_2CuO_3.

In the second step, mainly $Tl_2Ba_2CuO_6$ and $Tl_1Ba_2Ca\,Cu_2O_{4.5}$ were built up. These phases act as precursors in the next step, for the preparation of the "2223" and "22(2 − x)x3" phases which were built up at 1193 K. Finally, the powders were cooled to room temperature with a cooling rate of 1.6 K/min. At this important step a reaction between the 2223 phase and gaseous Tl_xO_y compounds takes place and the loss of thallium and oxygen can be reduced to a minimum. The samples have been characterized by the Guinier diffraction method ($Cu_{K\alpha 1}$ radiation). From the possible Tl-containing superconductive phases besides the 2223 and 2212 phases, small amounts of the 1223 phase could be identified. The samples with lower x values contained mainly the types 2223, 2212, and small amounts of 1223. The X-ray characterization showed that besides the lines of the superconductive phases, lines of the paramagnetic phase $BaCuO_2$ were also present. For higher x values ($x \geq 0.3$) the number of lines of unidentified phases increased whereas the contribution of the superconductive phases considerably decreased. The trends observed qualitatively in the X-ray characterization were, as is shown later, confirmed by the analysis of the magnetic measurements. In connection with the results of the X-ray analysis it is worth mentioning that in the X-ray diagram of the sample with the nominal composition $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ ($x = 0$) in the range $4.87° < 2\theta < 62.11°$ only lines of the 2223 phase were present. Nevertheless we found from the analysis of the magnetic measurements evidence for the superconductive 2212 phase and the paramagnetic $BaCuO_2$.

Because of their similar ionic character and ionic radii (93 pm for Y^{3+} and 99 pm for Ca^{2+}) one can expect that a substitution of Y for Ca is possible. It is important to note that the Tl^{3+} ionic radius (95 pm) is also similar to that of Y^{3+} and therefore there are, at least, two ionic sites, of Ca^{2+} and Tl^{3+}, where Y can be inserted. Using the Biltz volume increment method (13), a theoretical dependence for the two lattice parameters c and a versus x can be obtained. In the case of the substitution of a smaller Y^{3+} on a Ca^{2+} site one should expect a slight decrease in the c parameter (~10 pm) and an increase in the a parameter with increasing x in the range $0 \leq x \leq 0.6$ reflecting a reduction in the equilibrium oxidation state of the CuO_2 sheets (decrease of the hole density). Because the volume increments of Y^{3+} and Tl^{3+} are equal the lattice parameter should not change in the case Y occupies Tl sites. Unfortunately the variations in the c and a lattice parameter are, in fact, very small, < ~ 10 pm, below the sensitivity of the Guinier diffractometer used, and therefore our X-ray characterization did not allow us to distinguish between the two possibilities.

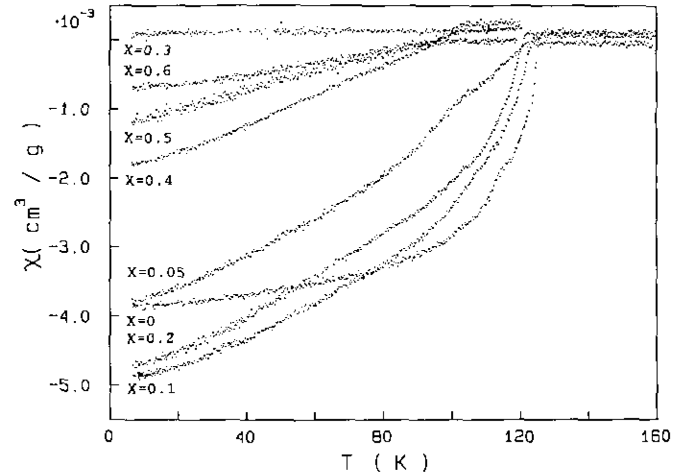

FIG. 1. The zero-field-cooled (zfc) temperature dependence of the magnetic susceptibility in low magnetic fields ($B = 1$ mT) for the ceramic $Tl_2Ba_2Ca_{2-x}Y_xCu_3O_{10+\delta}$ ($0 \leq x \leq 0.6$) compounds.

3. MAGNETIC MEASUREMENTS

The onset of superconductivity was detected by measurements of the magnetic moment. The magnetic measurements were performed with a sensitive home-made vibrating sample magnetometer (VSM) with a resolution of $\Delta M \sim 5 \times 10^{-8}$ Am^2 (= 5×10^{-5} emu) in fields up to 1.5 T and at temperatures between 4 and 300 K using heating rates of about 3 K/min. All the samples had the same cylindrical shape with a thickness of 2 mm and a 4-mm diameter. The temperature dependence of the magnetic susceptibility for the samples designated by their nominal Y^{3+} content x measured at 1 mT low field in both zfc and fc regimes is shown in Figs. 1 and 2. A closer inspection of Fig. 2 shows that as expected from the re-

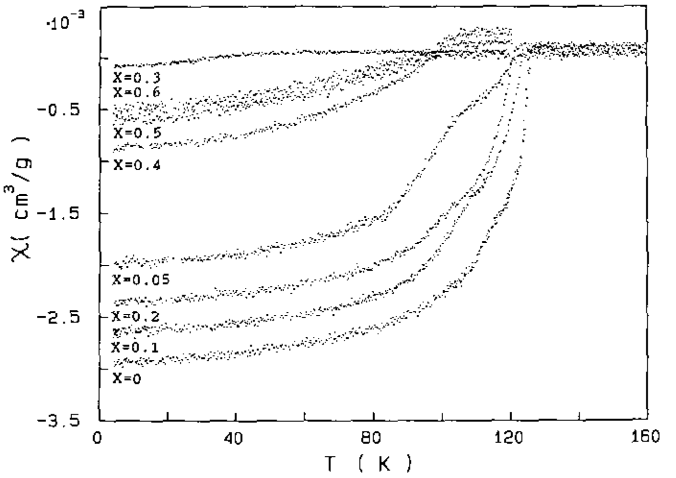

FIG. 2. The field-cooled (fc) temperature dependence of the magnetic susceptibility in low magnetic fields ($B = 1$ mT) for the ceramic $Tl_2Ba_2Ca_{2-x}Y_xCu_3O_{10+\delta}$ ($0 \leq x \leq 0.6$) compounds.

sults of the X-ray analysis there is evidence for two superconducting transitions characterized by two different critical temperatures, a higher one T_{c1} (onset temperature) and a second lower one T_{c2}, which can be taken as corresponding to the 2223 and 2212 phases, respectively.

The first critical temperature T_{c1} of the 2223 phase can be better estimated than T_{c2} using the kink point method. For $0 \leq x \leq 0.2$, T_c decreases from 126 to 118 K, as it is shown in Fig. 3. However it is worth to notice that in Fig. 3 the magnitude of the error bars for $x < 0.3$ are in the order of the symbol dimension (i.e., 0.2–1 K). For $x > 0.3$ the transitions become very smooth and the estimation of T_c is more difficult. A critical temperature of 125 K is typical for the 2223 phase (10). With suitable annealing procedures even higher values up to 130 K (19, 27, 29) can be reached. Annealings in Ar atmosphere as we already performed have a positive influence on T_c, as shown recently by Kaneko *et al.* (30). Therefore, a T_c of 126 ± 1 K can be undoubtedly ascribed to the 2223 phase. At this point we would like to stress that the 126 K we obtained for the 2223 phase and the 114 K for the 2212 phase in the sample without yttrium have been obtained as onset temperatures by using our dc susceptibility data only.

The second (lower) critical temperature T_{c2} of the 2212 phase also given in Fig. 3 is even more difficult to determine because of the presence of the 2223 phase and the error bars reach much higher values than in the case of the determination of T_{c1} (~5 K). As in the case of T_{c1}, the critical temperature of the 2212 phase decreases slowly from about 114 to 100 K in the range $0 \leq x \leq 0.2$. At this point we can mention the results of Martin *et al.* (20), who find that Y or Nd substitutions for Ca in Tl-2212 up to $x = 0.2$ give rise to changes in T_c of about 10 K.

As previously mentioned we could see in the X-ray diagram of the sample with $x = 0$ practically only lines belonging to the 2223 phase. This result is at variance with the conclusion based on the analysis of the susceptibility measurement where a second superconducting transition occurred around 114 K. This discrepancy could be removed assuming that 114 K represents the critical temperature of a 2223 phase under another oxygen content, as the one with $T_c = 126$ K.

But for the other compositions with $0 < x < 0.3$, the X-ray diagrams offered clear evidence for the presence of the 2212 structure as a second phase. For this reason for the sake of continuity we would favor the interpretation that the phase with $T_c = 114$ K in the sample with $x = 0$ is probably a 2212 phase. Another argument can be found in the results presented by Martin *et al.* (20), who showed that annealings in Ar or Ar/H_2 can give rise to an increase of the critical temperature of the 2212 phase from 97 to 118 K.

Measurements in a higher field of 1.5 T, above T_c and far from the fluctuation regime ($T > T_c$) show, as can be seen from Fig. 4., a Curie–Weiss behavior originating most probably from the paramagnetic $BaCuO_2$ phase. For the estimation of the Curie constants we fitted the susceptibility above 150 K to

$$\chi(T) = \frac{C}{T - \Theta_P} + \chi_0$$

assuming that only the core diamagnetism χ_{core} and the temperature-independent Pauli susceptibility term χ_P contribute to χ_0. The molar Curie constants were determined from nonlinear least-squares fits. The obtained values shown in Fig. 5 seem to be rather large, but in fact if we

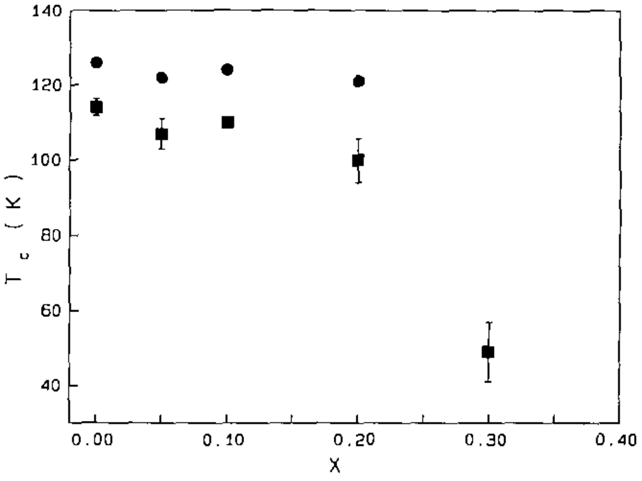

FIG. 3. Dependence of the critical temperature on the Y content x (■, for the 2212 phase; ●, for the 2223 phase).

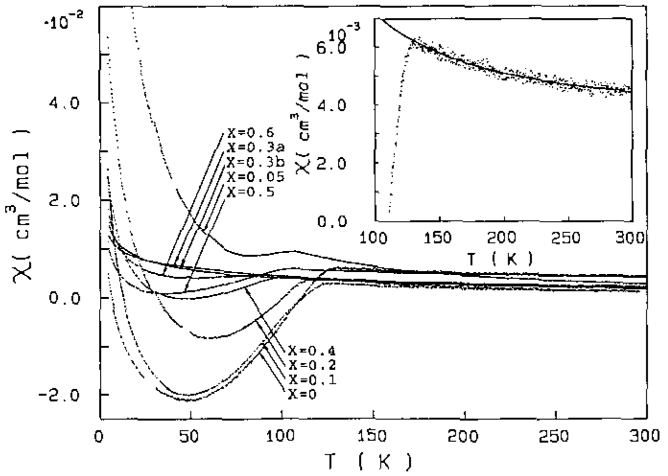

FIG. 4. Temperature dependence of the molar susceptibility at 1.5 T for different substitutions (for $x = 0.3$, two series of samples labeled a and b were prepared). The inset shows the magnetic susceptibility of the reference sample ($x = 0$) for $100\ \mathrm{K} \leq T \leq 300\ \mathrm{K}$ at 1.5 T. The solid curve represents a nonlinear least-squares fit to a Curie–Weiss behavior. The temperature-independent part of the susceptibility was subtracted before fitting.

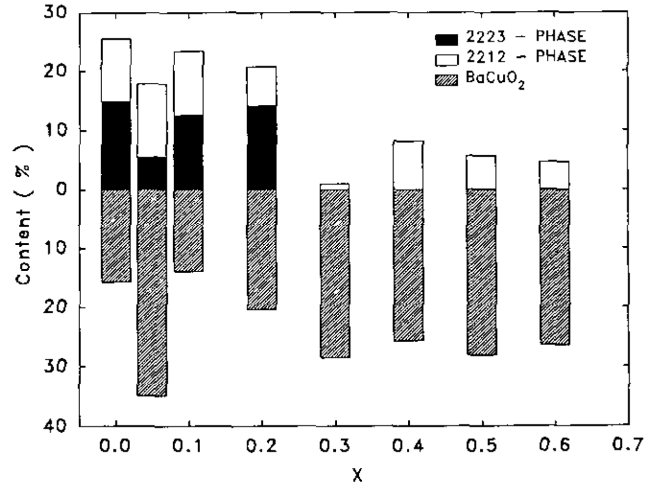

FIG. 6. The content of the Meissner fraction, 2223 phase, and 2212 phase versus the Y content x.

assume the contribution to the paramagnetic phase as arising from $BaCuO_2$ only, they correspond to an amount of ~20 mass% $BaCuO_2$ for $0 \leq x \leq 0.2$ and of ~27 mass% for $x > 0.2$. Our assumption is supported by the X-ray analysis, where several diffraction peaks could be identified with major $BaCuO_2$ lines. A detailed discussion about the magnetic identification of the impurity phase is made in the Appendix of Ref. (14).

In order to calculate the separate contributions of the 2223 and 2212 phases to the Meissner fraction, we took into account the demagnetization effect and therefore the data have been corrected with an estimated demagnetization factor $N = 1/3$ (S.I.) following the same arguments and procedure as in (14–17). Because of the high degree of porosity shown by these cuprates, the X-ray density calculated for the two phases was used in the definition of the magnetization per unit volume. The Meissner fraction found in the measurements at 1 mT amounts to about 20–30% of the total volume, as is usual the case with the Tl-containing HTSC. There are at least two reasons for such a behavior. First, the rather large amount of the Curie–Weiss paramagnetic phase (between 18 and 35 vol%) which is practically always present. Second, owing to the polycrystalline and highly porous structure strong field penetration can occur in very low fields, leading to the decrease of the Meissner fraction for the 1 mT used in the field-cooled regime.

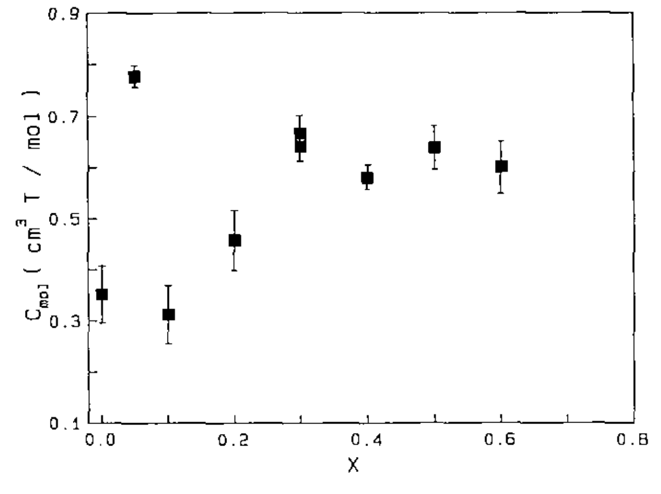

FIG. 5. The molar Curie constants for $T < T_c$ as function of the Y content x in the samples.

The relative amounts of the 2223, 2212, and $BaCuO_2$ phases as determined from the analysis of the susceptibility curves below and above T_c are shown in Fig. 6. For higher substitution rates $0.3 \leq x \leq 0.6$ the superconducting properties are seriously altered and drastic changes occur in the structure. As can be seen from Figs. 2 and 6, the Meissner fraction decreases drastically for $x > 0.2$ from a mean value of ~23% for $0 \leq x \leq 0.2$ to about 7% for $x > 0.3$, and even less than 1% for $x = 0.3$. For $x = 0.3$ we have prepared two series of samples labeled a and b and both of them showed the same peculiar behavior. As one can see from Fig. 4, only very small amounts of a superconducting phase are present which when corroborated with the low T_c values was identified with the Tl-2212 phase. In fact for $0.3 \leq x \leq 0.6$ we can conclude that the superconducting phase becomes unstable and therefore will not be formed except aleatory in some small amounts, due to the difficulty in controlling the preparation conditions of these compounds. These results are in agreement with the already reported behavior of Tl-2212, Bi-2212, and Bi-2223 compounds, in which lanthanide elements partially substitute Ca sites, the difference consisting only in the value of the "critical" Y content at which the superconductive phase becomes unstable. The high rates of substitution favor, due to the high volatility and the enhanced mobility (changes of the melting temperature) of thallium, the creation of various Tl compounds such as Tl_2O_3 and $TlBa_2Cu_2O_{5.5+x}$ and an increase in the amount of $BaCuO_2$ destabilizing the superconducting phases and practically hindering their formation.

4. DISCUSSION

The mechanism responsible for the high T_c superconductivity in the copper oxides appears to be restricted only to a narrow mixed-valent compositional range within the CuO_2 sheets (in which all the Cu atoms have an identical oxygen coordination and geometry). One of the necessary conditions to supress long-range antiferromagnetic order and induce superconductivity is the oxidation of the CuO_2 conducting sheets above the formal 2+ Cu valence, i.e., an increase in the copper valence or increase in the hole density (18–22, 26). For the presence of holes in the $Tl_2Ba_2Ca_{m-1}Cu_mO_{2m+4}$ several possible mechanisms have been proposed:

(1) excess oxygen in the Tl–O layers;

(2) presence of Tl vacancies and substitution of Tl with Ca;

(3) charge transfer $Tl^{+3-\Delta} \rightleftarrows Cu^{+2+\Delta'}$.

It is obvious that, as already mentioned in the Introduction for the case that no other mechanisms will interfere, a substitution of Y^{3+} for Ca^{2+} has to give rise to a reduction of the hole concentration and therefore influence the critical temperature T_c. Such substitutions were undertaken in the case of $Tl_2Ba_2CaCu_2O_8$ (24, 25). Poddar *et al.* (24) reported superconductivity in $Tl_2Ba_2Ca_{1-x}Y_xCu_2O_8$ for $x \leq 0.4$ and semiconducting behavior for $x \geq 0.48$. The critical temperature reached 85 K for $x = 0$ and 0.1 and then decreased quasilinearly to 30 K for $x = 0.48$. According to Martin *et al.* (20), T_c was about 103 K for $x = 0$, around 110 K for $x = 0.1$ and 0.2 and decreased to about 92 K for $x = 0.4$. In a similar study of Paranthaman *et al.* (25, 26) the T_c of the sample without Y ($x = 0$) reached 94 K and decreased to 72 K for $x = 0.2$. For $x > 0.3$ the superconductivity collapsed and the samples became semiconducting. The drastic change in the electrical properties for x values around 0.3 was accompanied by an important expansion of the lattice a parameter.

The main result of our study is that under our preparation conditions which lead to a T_c value of 126 K for the Tl-2223 compound, the attempt to substitute Y for Ca according to the starting composition $Tl_2Ba_2Ca_{2-x}Y_xCu_3O_{10+\delta}$ leads to a destabilization of the 2223 phase and to the formation of a high amount of the 2212 phase. For this reason it is not possible to try to find the hole concentration from the results of a chemical determination of the thallium and oxygen content as proposed by Paranthaman *et al.* in their study of the $Tl_{2-x-z}Ba_2Ca_{2+x}Cu_3O_{10-\delta}$ system (22). But, despite the presence of both superconducting phases 2223 and 2212 we have seen that, based on the susceptibility measurements, we could find the dependence of T_c on x in the range $0 < x \leq 0.2$ for both phases (Fig. 3). For a change $\Delta x = 0.2$ in the Y concentration (starting with $x = 0$) the critical temperature of the 2212 phase decreases by 14 K, whereas for the 2223 phase the reduction reaches only 8 K. We believe that this result arises from the substitution of Y^{3+} for Ca^{2+} in both superconducting phases. Our finding for the 2212 phase is in general agreement with the results of Martin *et al.* (20) and Paranthaman *et al.* (22) already mentioned before. However, we have to mention that under our conditions of preparation we reached for Tl-2212 in the reference composition a T_c value of 114 K, which is substantially higher than the 103 and 94 K reported in (24) and (25, 26), respectively. Therefore we are allowed to suppose that in our 2212 phase for $x = 0$ we are at (or close to) the optimal hole concentration, and the substitution of Y for Ca can only contribute to a reduction of both the number of holes and critical temperature. The same argument holds for the Tl-2223 phase with the difference that because of the critical temperature of 126 K for $x = 0$ we have to expect a slower decrease of T_c with x, in good agreement with our experimental data (Fig. 3).

One is tempted to compare the influence of Y substitutions on the superconducting properties of Tl-2223 with similar substitutions in Bi-2223 HTSC. Unfortunately, as already mentioned in the Introduction, the attempts to perform such kind of substitutions destabilize the Bi-2223 phase and only the superconductive 2212 phase occurs. Our results argue in favor of a higher stability of the Tl-2223 phase against substitutions, at least in the case of the incorporation of Y at the Ca sites up to $x = 0.2$. Above $x = 0.3$ the only superconductive phase practically present is 2212 in small amounts with T_c values varying nonsystematically in the range 90–104 K. We consider the presence of the 2212 phase as atypical and we believe that, as in the study of Paranthaman *et al.* (25, 26), the superconductive state is destabilized around $x = 0.3$, with the difference that in our case this happens also with the 2223 phase.

Besides the proposed explanation for the decrease of T_c based on the reduction of the concentration of holes owing to the substitution of Y and Ca, one can envisage as an alternative mechanism a systematic change in the oxygen concentration with increasing Y content in the starting compositions. Such a possibility cannot be neglected, but it would mean that Y does not substitute at all in the Tl-based 2223 and 2212 phases. But such a conclusion is in disagreement with the already mentioned papers of Martin *et al.* (20) and Paranthaman *et al.* (22) about the Y substitutions in the Bi- and Tl-based 2212 phase.

5. CONCLUSIONS

Starting from the nominal compositions $Tl_2Ba_2Ca_{2-x}Y_x Cu_3O_{10+\delta}$ under our specific preparation conditions, consisting mainly in the 12-h heat treatment at 1123 K followed by a short duration treatment of 15 min at 1193 K in Ar atmosphere, we obtained for $0 \leq x < 0.3$ samples containing both superconducting 2212 and 2223 phases with critical temperatures slightly decreasing with increasing Y content. Besides the superconducting phases, a Curie–Weiss paramagnetic phase, probably $BaCuO_2$, was always present.

The critical temperature of the 2223 phase decreased from 126 K for $x = 0$ to 118 K for $x = 0.2$, whereas for the 2212 phase the decrease is stronger, from 114 K for $x = 0$ to 100 K for $x = 0.2$. We believe that the change in T_c occurred from the partial substitution of Y for Ca in both 2212 and 2223 phases.

For $x > 0.3$, only small amounts of a superconductive phase, mostly 2212, and large amounts of the Curie–Weiss paramagnetic phase are present. It seems that the presence of higher amounts of Y_2O_3 in the nominal composition destabilizes the superconducting phases.

ACKNOWLEDGMENTS

The financial support of the Bundesministerium für Forschung und Technologie (Project 13N5713) and also the financial support for D.-N. Peligrad from the Deutscher Akademischer Austauschdienst are gratefully acknowledged. We thank R. Job, M. Mittag, and R. Wernhardt for many useful discussions.

REFERENCES

1. W. A. Groen and D. M. Leeuw, *Physica C* **159,** 417 (1989).
2. B. Chevalier, B. Lepine, A. Le Lirzin, J. Darriet, and J. Etourneau, *Mater. Sci. Eng.*, preprint.
3. R. Yoshizaki, H. Kurahashi, N. Ishikawa, M. Akamatsu, J. Fujikami, and H. Ikeda, *in* "Proceedings of the Tsukuba Seminar on High T_c Superconductivity, May 31–June 22, 1989."
4. I. Nowik, I. Felner, and E. R. Bauminger, *Phys. Rev B* **45,** 4912 (1991).
5. Y. Gao, P. Pernambuco-Wise, J. E. Crow, J. O'Reilly, N. Spencer, H. Chen, and R. E. Salomon, *Phys. Rev. B* **45,** 7436 (1992).
6. K. Koyama, S. Kanno, and S. Noguchi, *Jpn. J. Appl. Phys.* **28**(8), 1354 (1989).
7. W. A. Groen, D. M. Leeuw, and L. F. Feiner, *Physica C* **165,** 55 (1990).
8. C. N. R. Rao, R. Nagarajan, R. Vijayaraghavan, N. Y. Vasanthacharya, G. V. Kulkarni, G. Ranga Rao, A. M. Umarji, P. Somasundaram, G. N. Subbanna, A. R. Raju, A. K. Sood, and N. Chandrabhas, *Supercond. Sci. Technol.* **3,** 242 (1990).
9. R. Job, M. Mittag, M. Rosenberg, A. V. Niculescu, B. Himmerich, and H. Sabrowsky, *Physica C, in* press.
10. S. S. Parkin, V. Y. Lee, A. I. Nazzal, R. Beyers, and S. J. La Placa, *Phys. Rev. Lett.* **61,** 750 (1988).
11. J. Mirza and H. Sabrowsky, *Naturwissenschaften* **64,** (1977).
12. P. G. Wahlbeck, R. D. Richards, and D. L. Myers, private communications.
13. W. Biltz "Raumchemie der festen Stoffe." Leopold Voss-Verlag Leipzig, 1934.
14. R. Job, M. Rosenberg, and A. V. Niculescu, *Physica C* **193,** 117 (1992).
15. W. Reith, P. Müller, C. Allgeier, R. Hoben, J. Heise, J. S. Schilling, and K. Andres, *Physica C* **156,** 319 (1988).
16. Y. Wolfus and Y. Yeshurun, *Phys. Rev. B* **16,** 11690 (1989).
17. D. M. Ginsberg (Ed.), "Physical Properties of High Temperature Superconductors," Vol. II, Chap. 3. World Scientific Singapore, 1989, and references cited therein.
18. M. Kikuchi, T. Kajitani, T. Suzuki, S. Nakajima, K. Hiraga, N. Kobayashi, H. Iwasaki, Y. Syono, and Y. Muto, *Jpn. J. Appl. Phys.* **28**(3), L382 (1989).
19. R. M. Iyer, G. M. Phatak, K. Gangadharan, M. D. Sastry, R. M. Kadam, P. V. P. S. S. Sastry, and J. V. Yakhimi, *Physica C* **160,** 155 (1989).
20. C. Martin, A. Maignan, J. Provost, C. Michel, M. Hervieu, R. Tournier, and B. Raveau, *Physica C* **168,** 8 (1990).
21. A. Manthiram, M. Paranthaman, and J. B. Goodenough, *Physica C* **171,** 135 (1990).
22. M. Paranthaman, M. Foldeaki, and A. M. Hermann, *Physica C* **192,** 161 (1992).
23. S. Nakajima, M. Kikuchi, Y. Syono, N. Kobayashi, and Y. Muto, *Physica C* **168,** 57 (1990).
24. A. Poddar, P. Mandal, A. N. Das, and B. Ghosh, *Phys. Rev. B* **44,** 2757 (1991).
25. M. Paranthaman, A. Manthiram, and J. B. Goodenough, *J. Solid State Chem.*, in press.
26. M. Paranthaman, A. Manthiram, and J. B. Goodenough, *in* "Thallium-Based High Temperature Superconductors" (A. M. Hermann and J. V. Yakhmi, Eds.). Dekker, New York, 1992.
27. S. Adachi, K. Mizuno, K. Setsum, and K. Wasa, *Physica C* **171,** 593 (1990).
28. T. Kaneko, H. Yamauchi, and S. Tanaka, *Physica C* **178,** 377 (1991).
29. R. S. Liu, J. L. Tallon, and P. P. Edwards, *Physica C* **182,** 119 (1991).
30. T. Kaneko, K. Hamada, S. Adachi, and H. Yamauchi, *Physica C* **197,** 385 (1992).