



## Preparation of pure $Tl_2Ba_2CuO_{6+x}$ : the contribution of phase equilibrium studies

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### Abstract

The formation of the pure thallium-based cuprate  $Tl_2Ba_2CuO_{6+x}$  (2201) using a convenient process in the ternary  $TlO_{1.5}$ -BaO-CuO phase diagram is described. This process is based on the congruent formation of the oxide  $Tl_2Ba_2O_5$  to which CuO is mixed, constituting a quasi-binary system. In the resulting 2201 compound no trace of the main poisoning magnetic impurity  $BaCuO_2$  could be detected by AC susceptibility measurements. The orthorhombic to tetragonal transformation is asserted to be due to thallium deficiency which occurs during the heat treatments at a temperature depending on the oxygen partial pressure.

### 1. Introduction

Despite possible problems related to the toxicity of thallium and its compounds, the superconducting properties of the thallium-based cuprates have been extensively studied. The review of Greenblatt et al. [1] reports more than 25 investigated Tl-based systems.

Actually, since the initial work of Sheng and Hermann [2] the thallium cuprates have the highest superconducting transition temperature,  $T_c$ , recently enhanced up to 130 K for  $Tl_2Ba_2Cu_3O_{10}$  by Kaneko et al. [3]. The first member of the two TlO-layers series  $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$  with  $n=1$ , referred to here as "2201", is particularly interesting. First, the compound is reported to undergo a structural transformation from orthorhombic to tetragonal symmetry [1,4-8] but the nature of the transition remains to be clarified. Relations between the transformation temperature and the oxygen and thallium content are unknown. Very recently Shimakawa et al. [9] suggested that the transition is composition dependent but quantitative effects

have not been determined. Secondly, whereas the tetragonal form is known to become superconducting with  $T_c$  scaling up to 95 K [5], there are some doubts about the superconductivity of the orthorhombic form.

In reality, the difficulty to obtain definitive results is obviously related to the difficulty to reproduce well defined  $Tl_2Ba_2CuO_{6+x}$  samples starting with the elemental compounds CuO or  $Cu_2O$ , BaO,  $BaO_2$  or  $BaCO_3$  and  $Tl_2O_3$ . The difficulties not only concern the thallium and oxygen stoichiometries but also the formation, during the first stages of the sintering process, of impurity phases.  $BaCuO_2$  especially cannot be completely eliminated, as observed in several studies [10,11], without a high temperature treatment. This in turn affects the thallium composition. In most cases, the amount of impurity phases is relatively low (1-3 vol.%) so that it cannot be detected by conventional X-ray diffraction techniques. The inconsistency between the usually claimed purity and the volume of superconducting phase is thus a puzzling problem.

In this paper we report a method to prepare "2201" at atmospheric pressure, which avoids the formation of  $\text{BaCuO}_2$  and allows one to obtain reproducible thallium concentrations. The orthorhombic to tetragonal transformation is confirmed to be due to thallium departure. The low temperature AC susceptibility of normal and superconducting  $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+x}$  is used as a purity test.

## 2. Experimental

The "2201" samples used in this study have been prepared with  $\text{Tl}_2\text{Ba}_2\text{O}_5$  ("2200") precursor. In our previous work on the  $\text{TlO}_{1.5}$ -BaO system [12] we found that  $\text{Tl}_2\text{Ba}_2\text{O}_5$  is a congruent melting compound at  $1080^\circ\text{C}$  with moderate  $\text{Tl}_2\text{O}_3$  vaporization before melting. Thus, the thallium stoichiometry of "2201" may be controlled during the sintering process. Powdered "2200" and a convenient amount of CuO (Rhone-Poulenc, 99.9%) have been mixed and fired at  $850^\circ\text{C}$  for 5 min and, after compaction sintered at  $630^\circ\text{C}$  for 70 h in flowing oxygen. The resulting weight losses, about 2% for 400-500 mg samples were reduced to 0.4% for samples of 4-5 g. The weight change and phase transition were determined by use of a Setaram TAG24 apparatus allowing one to perform simultaneous differential thermal analysis and thermo-gravimetry (DTA/TG) measurements in controlled atmospheres (He, Ar,  $\text{O}_2$ ).

The orthorhombic to tetragonal phase transition was also investigated by high temperature X-ray diffraction (XRD) in the range  $2\theta = 31$ - $34$  degrees including the orthorhombic doublet (200)-(020). The room temperature XRDs were recorded with a Siemens D520 powder diffractometer. The composition has been controlled either by grain analysis with an energy dispersive X-ray system attached to a scanning electron microscope (SEM/EDX) or by plasma emission spectroscopy. The thallium content was obtained from chemical analysis using a procedure described by Paranthanam et al. [13]. The low temperature behaviour of the samples was studied by AC susceptibility. The method is

efficient in investigating magnetic properties and thus may be used to detect magnetic impurities at a low level. It is also a powerful tool to study in detail the bulk superconductivity [14,15].

## 3. Results and discussion

### 3.1. Phase formation

As already mentioned  $\text{Tl}_2\text{Ba}_2\text{O}_5$  is a congruent melting compound at  $1080 \pm 20^\circ\text{C}$ . A monoclinic distortion of an orthorhombic type structure has been proposed for the compound by Zhou et al. [16] but all the diffraction lines observed in our "2200" master samples could be indexed assuming an orthorhombic symmetry with the lattice parameters  $a=6.226(4)\text{\AA}$ ,  $b=6.047(7)\text{\AA}$  and  $c=17.179(5)\text{\AA}$ . In an oxygen atmosphere of 1 bar, the decomposition of CuO occurs at  $1120^\circ\text{C}$  [17]. The  $\text{Tl}_2\text{Ba}_2\text{O}_5$ -CuO system is a quasi-binary system and except along an invariant line, no ternary equilibrium should be observed. The composition must be solely a combination of  $\text{Tl}_2\text{Ba}_2\text{O}_5$  and CuO. Figure 1 shows the direct reaction of powdered "2200" and CuO in the DTA cell. The two endotherms at  $880^\circ\text{C}$  and  $920^\circ\text{C}$  are due to the eutectic plateau and the liquidus respectively, at a composition close to "2201".

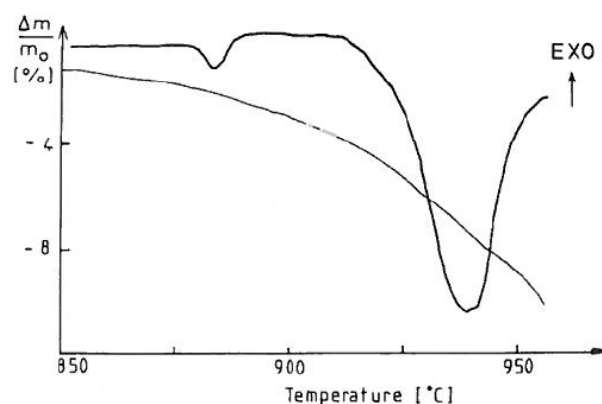


Fig. 1. Direct formation in the DTA/TG apparatus of  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  showing the reduced weight losses (4%) preceding the melting of the sample at  $930^\circ\text{C}$ .

The formation reaction of the mixed oxide cannot be observed but from isothermal experiments we found that a flash heat treatment

at 850°C improved the efficiency of "2201" formation. From the TG curve in fig. 1, it may be seen that the thallium content is not significantly changed before the melting of the sample, allowing one to obtain an accurate control of the composition and a drastic reduction of toxicity problems.

Formation from the liquid state appears in fig. 2 which is the quasi - binary section extracted from the study of the ternary system  $\text{TlO}_{1.5}\text{-BaO-CuO}$  [18].

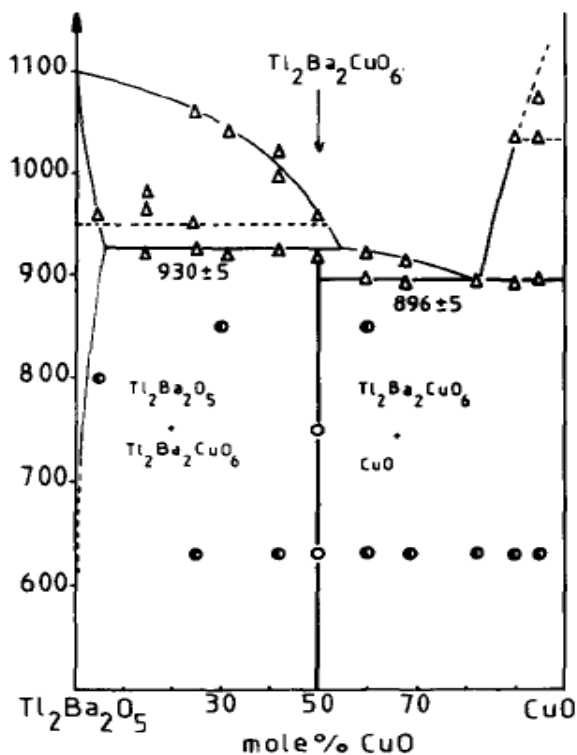


Fig. 2 The quasi-binary section  $\text{Tl}_2\text{Ba}_2\text{O}_5\text{-CuO}$ , where ( $\Delta$ ) is DTA, (O) single phase by XRD, and ( $\bullet$ ) two-phase.

$\text{Tl}_2\text{Ba}_2\text{CuO}_6$  is shown to be formed by the peritectic reaction:  $\text{Tl}_2\text{Ba}_2\text{O}_5 + \text{liquid} \rightarrow \text{Tl}_2\text{Ba}_2\text{CuO}_6$  at  $930 \pm 5^\circ\text{C}$ .

DTA/TG of orthorhombic "2201" reveals that in our experimental conditions, in flowing oxygen, the thallium stoichiometry at the peritectic temperature is decreased to 1.9, assuming  $\text{Tl}_2\text{O}_3$  departure. At this level of thallium vacancy, no solid-state phase transition was observed, neither by DTA nor by XRD analysis of quenched specimens, indicating that the material remains orthorhombic. The results are consistent with the neutron scattering data of Hewat et al. [6] showing that the orthorhombic "2201" accepts up to 12.5% thallium deficiency. Moreover, they

suggest that the transition from orthorhombic to tetragonal-type structure is not a simple temperature dependent transformation.

### 3.2. The tetragonal phase formation

In the literature there is a general agreement concerning the formation of a tetragonal  $\text{Tl}_2\text{Ba}_2\text{CuO}_z$  which is obtained, as summarized in table 1, after various heat treatments of the orthorhombic form. However, the transition is not clearly described and has been considered with a microscopic approach. Bordet et al. [20], on the basis of electron diffraction experiments associated the tetragonal symmetry to short-range ordering whereas Manthiram et al. [21] argued an ordered extrusion of "TlO" units for describing the orthorhombicity of the 2201 compound. In fact the formation of tetragonal 2201 also has to be considered from a thermodynamic viewpoint, on the basis of a phase diagram. We have already mentioned that in samples prepared using  $\text{Tl}_2\text{Ba}_2\text{O}_5$  as precursor the thallium stoichiometry may be decreased to 1.9 without affecting the orthorhombicity. From accurate TG measurements we found that the formation of the tetragonal form implies thallium oxide departure which, following the recent work of Walhbeck et al. [22], is here assumed to be  $\text{Tl}_2\text{O}_3$ . All the Tl compositions after the various heat treatments hereafter reported have been calculated using this assumption and noting that, for a molecular weight of 843 g of  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ , one  $\text{TlO}_{1.5}$  unit corresponds to 27.1 weight%. The starting master samples with a typical weight of 400 mg were orthorhombic with the lattice parameters:  $a=5.432(5) \text{ \AA}$ ,  $b=5.493(5) \text{ \AA}$ ,  $c=23.12(1) \text{ \AA}$ . From plasma emission analysis, the thallium content was 1.9, in agreement with weight loss measurements.

In static or flowing oxygen atmospheres the tetragonal symmetry can be obtained by annealing an orthorhombic 2201 specimen above 800°C for times depending on sample size. Alternatively, a deficient Tl material may be directly prepared. Our study on the ternary  $\text{TlO}_{1.5}\text{-BaO-CuO}$  system [18] showed that the 2201 specimens were orthorhombic except for

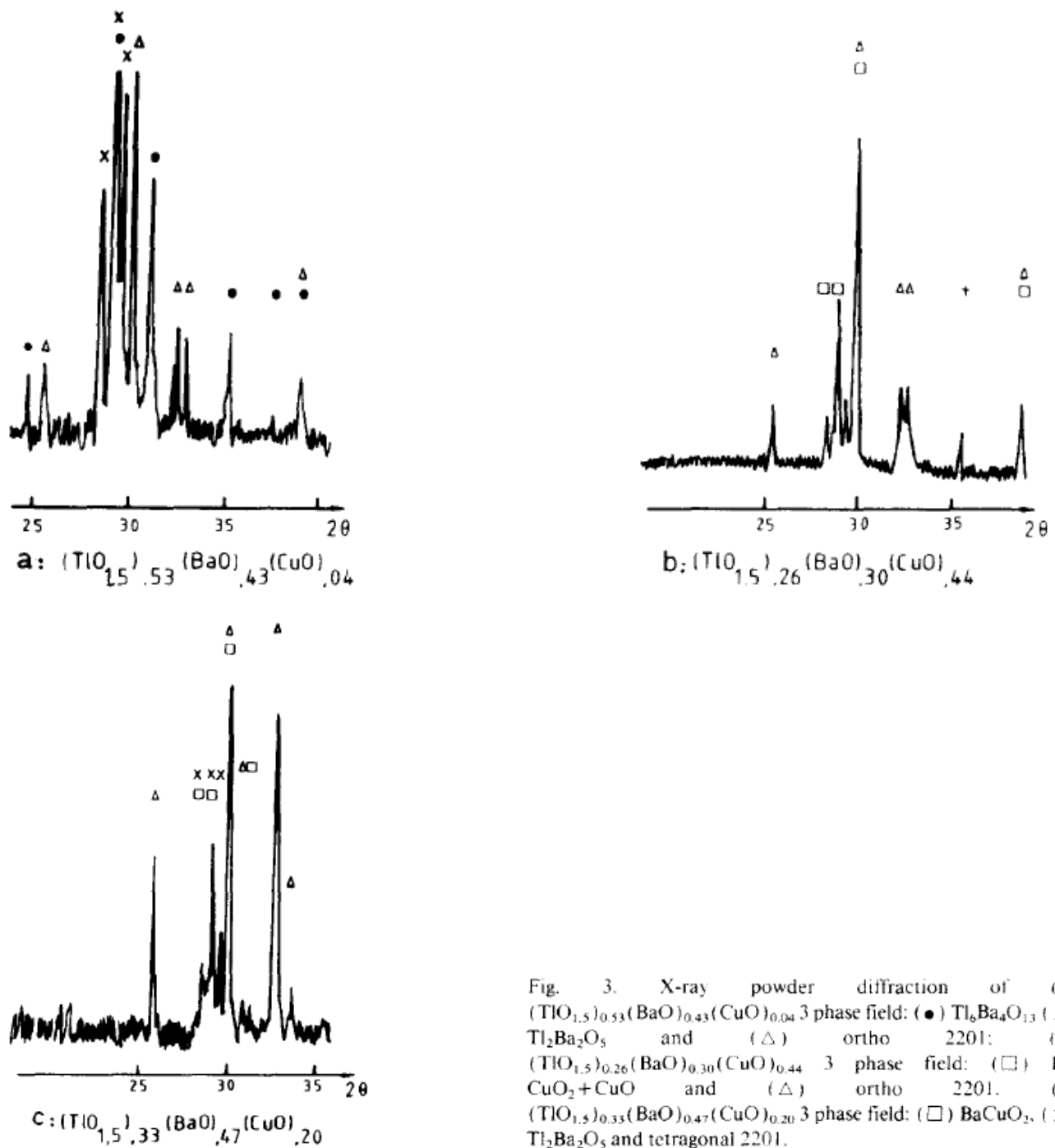


Fig. 3. X-ray powder diffraction of (a)  $(\text{TlO}_{1.5})_{0.53}(\text{BaO})_{0.43}(\text{CuO})_{0.04}$  3 phase field: (●)  $\text{Tl}_6\text{Ba}_4\text{O}_{13}$  (×)  $\text{Tl}_2\text{Ba}_2\text{O}_5$  and (Δ) ortho 2201; (b)  $(\text{TlO}_{1.5})_{0.26}(\text{BaO})_{0.30}(\text{CuO})_{0.44}$  3 phase field: (□)  $\text{BaCuO}_2 + \text{CuO}$  and (Δ) ortho 2201. (c)  $(\text{TlO}_{1.5})_{0.33}(\text{BaO})_{0.47}(\text{CuO})_{0.20}$  3 phase field: (□)  $\text{BaCuO}_2$ , (×)  $\text{Tl}_2\text{Ba}_2\text{O}_5$  and tetragonal 2201.

those belonging to the ternary  $\text{Tl}_2\text{Ba}_2\text{O}_5 + \text{BaCuO}_2 + 2201$  phase field which presented the tetragonal symmetry. Figure 3 represents the XRD patterns of  $(\text{TlO}_{1.5})_{0.53}(\text{BaO})_{0.43}(\text{CuO})_{0.04}$  in the three phase field  $\text{Tl}_6\text{Ba}_4\text{O}_{13} + \text{Tl}_2\text{Ba}_2\text{O}_5 +$  orthorhombic  $\text{Tl}_2\text{Ba}_2\text{CuO}_z$  (fig. 3(a)), of  $(\text{TlO}_{1.5})_{0.26}(\text{BaO})_{0.30}(\text{CuO})_{0.44}$  in the field  $\text{CuO} + \text{BaCuO}_2 +$  orthorhombic  $\text{Tl}_2\text{Ba}_2\text{CuO}_z$  (fig. 3(b)) and finally  $(\text{TlO}_{1.5})_{0.33}(\text{BaO})_{0.47}(\text{CuO})_{0.20}$  in

the  $\text{Tl}_2\text{Ba}_2\text{O}_5$ ,  $\text{BaCuO}_2$  and tetragonal "2201" field (fig. 3(c)). These results contradict the usually accepted [1] reversibility of the orthorhombic-tetragonal transformation with the temperature. Actually *inversibility* may be ascertained by taking into account the change in composition. We have found that departure of 0.1 mole of  $\text{TlO}_{1.5}$  from the initial  $\text{Tl}_{1.9}\text{Ba}_2\text{CuO}_z$  promoted tetragonal "2201" which should be described as  $\text{Tl}_{1.8}\text{Ba}_2\text{CuO}_z$ . Heat treating such tetragonal compound in flowing oxygen did not

change the structure up to 915°C, the melting temperature, slightly lower than for orthorhombic "2201" (fig. 4). From 850°C to 910°C the weight losses were reduced to 1.3% i.e. 0.05  $\text{TlO}_{1.5}$ , the sample remaining tetragonal, suggesting a small homogeneity range in the  $\text{TlO}_{1.5}$  direction which extends to  $\text{Tl}_{1.7}\text{Ba}_2\text{CuO}_z$ . From that composition, pure orthorhombic "2201" could be recovered solely by addition of  $\text{Tl}_2\text{O}_3$  followed by annealing at 650°C thus showing the inversibility of the reaction.

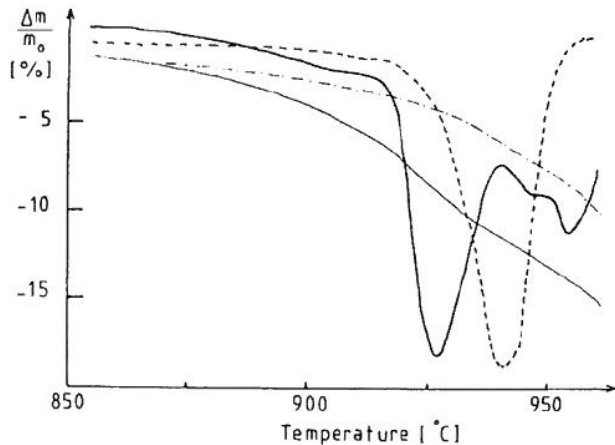


Fig. 4. DTA of 2201 samples showing (---) the peritectic plateau at 930°C corresponding to the melting of ortho 2201 containing 1.9 Tl, deduced from the weight change (-.-.-). The liquidus is found at 940°C. (—) is the melting of tetragonal 2201 containing, from the TG curve (---), 1.77 Tl at 915°C.

In an oxygen free atmosphere ( $10^{-2}$  mbar, flowing argon or helium), thallium losses occur at temperatures as low as 500°C. Figure 5 represents the evolution of the XRD pattern in helium of orthorhombic "2201" as the temperature is increased. From room temperature to 500°C, the characteristic diffraction lines (020), (200) of the orthorhombic structure are separated by  $2\theta = 0.37(2)^\circ$ . At 630°C, the (200) peak seems to merge into (020) but the (110) diffraction line of the tetragonal structure is apparent, suggesting the existence of a two-phase field between tetragonal and orthorhombic "2201". The reaction is complete at 670°C and simultaneously,  $\text{BaCuO}_2$  appears as minor phase, increasing with time and reflecting compositional change. From the (200), (020) and (115) diffraction lines of orthorhombic "2201"

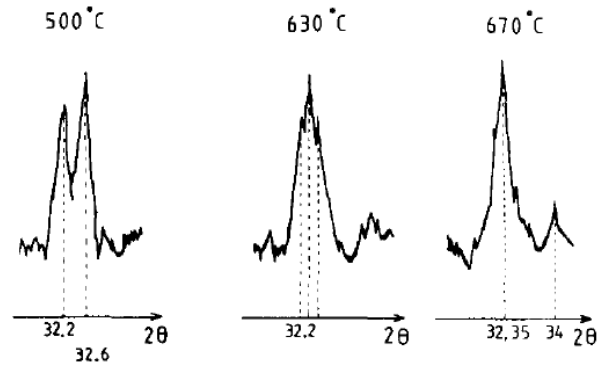


Fig. 5. High-temperature X-ray powder diffraction of ortho 2201 in helium: (a)  $T=500^\circ\text{C}$ : the (020) and (200) doublet of ortho 2201; (b)  $T=630^\circ\text{C}$ : growth of tetragonal 2201. One finds evidence that the sample at this temperature is two-phase; (c)  $T=670^\circ\text{C}$ : tetragonal (110) diffraction line. The formation of  $\text{BaCuO}_2$  as impurity may be observed at  $2\theta=33.85^\circ$ .

and the (110) and (105) lines of the tetragonal form we deduced the thermal expansion of the lattice parameters. Figure 6 shows a linear temperature dependence of the orthorhombic parameters  $a_o(T)$  and  $b_o(T)$ . The slight difference between the thermal expansion coefficients  $\alpha_a = 14.2 \times 10^{-6} \text{ K}^{-1}$  and  $\alpha_b = 13.5 \times 10^{-6} \text{ K}^{-1}$  reflects the stability of the Tl-O (3) slab which produces the orthorhombicity, thus extending to high temperatures the results of Parise et al. [23] who studied the low temperature range  $12 \text{ K} < T < 293 \text{ K}$ . Note that the thermal expansion does not differ too much from the values for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , as deduced from the study of Jorgensen et al. [24]. However, in the case of thallium based 2201, the orthorhombic  $a_o$  and  $b_o$  do not converge to a "virtual"  $a_{\text{tetra}}$  obtained from the real lattice  $a_T$  by  $a_{\text{tetra}} = \sqrt{2}a_T$  which seems to follow a similar temperature dependence. Owing to the stability of the two TlO layers, relative to thallium vacancies, there is no discontinuity in the c-direction between orthorhombic and tetragonal cells and thus, a linear orthorhombic and tetragonal cells and thus, a linear volume-temperature dependence is observed, with a volume thermal expansivity  $\beta = 39.4 \times 10^{-6} \text{ K}^{-1}$ . We argue that orthorhombic and tetragonal  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  are two ordered phases which may be schematically represented in the enlarged phase diagram on fig. 7. In table 2 we report the sample analyses which supports our conclusions.

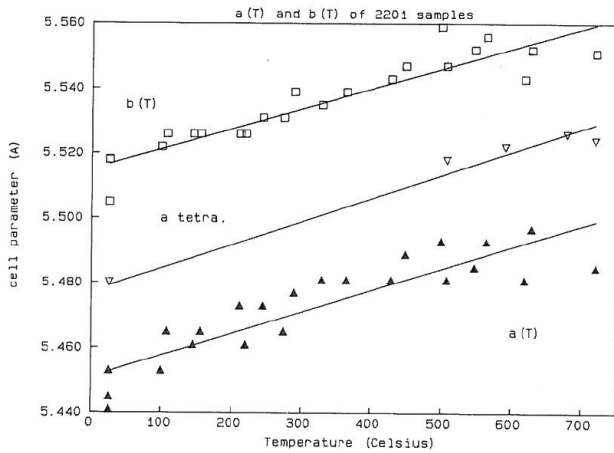


Fig. 6. The linear temperature dependence of the cell parameters of the ortho and tetra 2201 deduced from high-temperature XRD in He. Note the coexistence of the two phases above 500°C. The low temperature value of a of the tetragonal cell suggests similar expansion as for the ortho parameters. The accuracy is affected by the temperature precision ( $\pm 50^\circ\text{C}$ ).

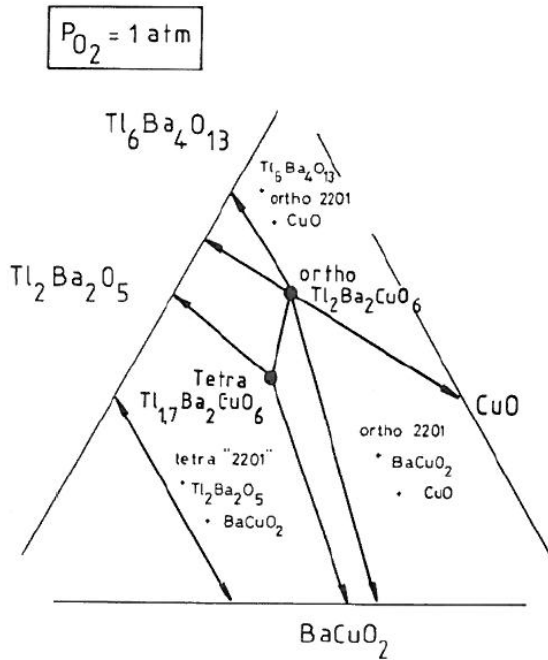


Fig. 7. Enlarged phase diagram at the vicinity of the 2201 phase.

The thallium contents were deduced by the determination of the weight loss and have been confirmed for samples (I) and (I + II) by wet chemical analysis and plasma emission spectroscopy which provided the compositions  $(\text{TlO}_{1.5})_{1.91}(\text{BaO})_2(\text{CuO})_{1.12}$  and  $(\text{TlO}_{1.5})_{1.74}(\text{BaO})_2(\text{CuO})_{1.11}$  respectively. Nevertheless, it should be interesting to complement this thermodynamic approach by careful investigations on the crystallographic structure of

Table 2  
Sample analysis reflecting the formation of tetragonal  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$

Preparation	Thallium content	Cell (Å)	$T_c$ (K)
I	1.93 <sup>a)</sup>	$a=5.432(5)$ $b=5.493(5)$ $c=23.12(1)$	NS
I+II	1.83	$a=3.851(3)$ $c=23.12(3)$	<4.2
I+II 500°C/2H/argon	1.83	$a=3.855(1)$ $c=23.03(3)$	53
I+II+500°C/2H +475°C/2H $P(\text{O}_2)=5 \times 10^{-2}$ atm	1.77	$a=3.855(1)$ $c=23.15(3)$	50
Item+ 475°C/38H/Ar(t)	1.77	$a=3.861(1)$ $c=23.15(2)$	22
I+475°C/2H $P(\text{O}_2)=5 \times 10^{-2}$ atm	1.77	$a=3.861(4)$ $c=23.15(2)$	53
I+650°C/DTA $P(\text{O}_2)=5 \times 10^{-2}$ atm	1.75	$a=3.876(5)$ $c=23.16(6)$	NM
I+650°C/DTA +0.3(TlO <sub>1.5</sub> ) +I	1.95	$a=5.451(4)$ $b=5.508(4)$ $c=23.21(2)$	NS

<sup>a)</sup> Resulting from plasma spectroscopy and chemical analysis; I is the preparation treatment: 630°C-10 h + 850°C-5 min followed by 630°C for 10 h in oxygen flowing, II is 900°C in encapsulated tubes under 3 atm of oxygen (t) encapsulated tube. NS denotes not superconducting, NM not measured.

the tetragonal phase. We have to note that a study of our samples by high-resolution electron microscopy is in progress [25].

### 3.3. Superconductivity

The magnetic susceptibility of the samples has been measured in the temperature range 1.2-150 K. As a general trend, the absolute value of about  $10^{-4}$  SI is in agreement with previous results of Junod et al. [26]. Superconductivity was not observed in samples with the orthorhombic-type structure. However, the latter revealed an interesting low temperature behavior. The magnetic susceptibility of orthorhombic "2201" is reduced remarkably for  $T < 50$  K (fig. 8) and remains unchanged when a static magnetic field (up to 1.5T) is superimposed on the AC field. This last experiment demonstrates that this behavior does not originate in superconductivity but reflects an intrinsic property such as magnetic ordering. In addition, the susceptibility measurement confirms the phase diagram expectation.  $\text{BaCuO}_2$  cannot be produced in the quasi-binary

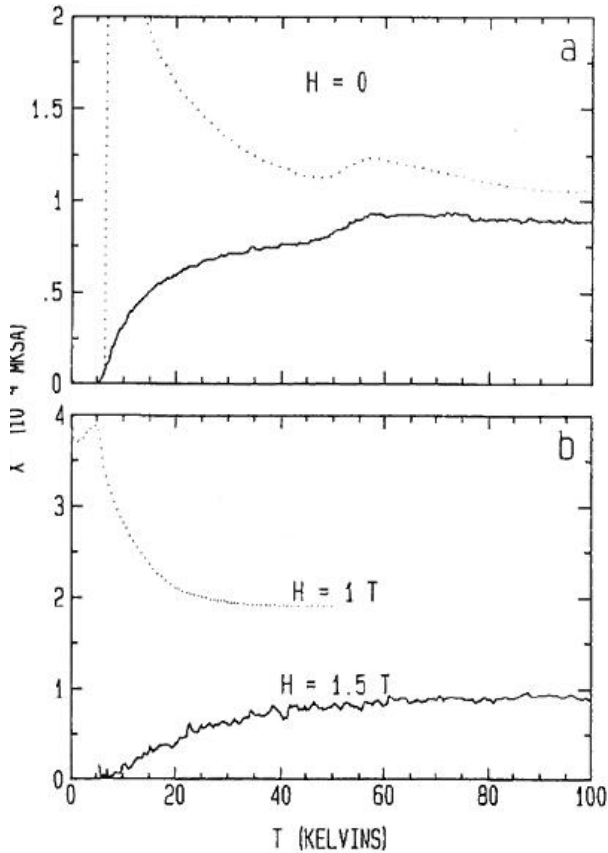


Fig. 8. AC susceptibility of 2201 samples.  $H_{AC}=35$  Oe (--) ortho 2201, The lowering of  $\chi'$  is not destroyed by a static superimposed field up to 1.5T and thus does not correspond to superconductivity; (....) tetra 2201. The large positive contribution preceding the superconducting transition at about 6 K is due to  $BaCuO_2$ . Superconductivity is destroyed by a superimposed DC field of 1 T.

$Tl_2Ba_2O_5-CuO$  system. The AC susceptibility of  $BaCuO_2$ , displayed in fig. 9, shows a positive contribution, decreasing with a superimposed DC field. This does not appear, at ppm levels in orthorhombic "2201" samples. However, it has to be mentioned that a small deviation from ideal thallium stoichiometry might produce  $BaCuO_2$  traces (see fig. 7) and thus modify the behavior. There is clear evidence of this during the formation of the tetragonal phase from orthorhombic samples by thallium losses, implying an inhomogeneous composition which may result in the presence of  $BaCuO_2$  as a minor impurity (in the range of  $10^{-2}$ - $10^{-3}$  vol.%). In fact, for tetragonal "2201" a positive contribution to the AC susceptibility preceding superconductivity is observed. This is shown in fig. 8 for a sample with a superconducting transition

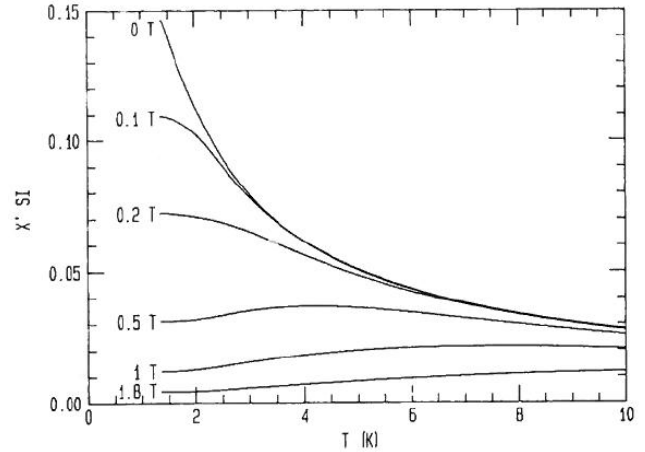


Fig. 9. AC susceptibility of  $BaCuO_2$  prepared in oxygen flowing at  $960^\circ C$ .  $H_{AC}=35$  Oe. The parameter is an external static field up to 1.8T.

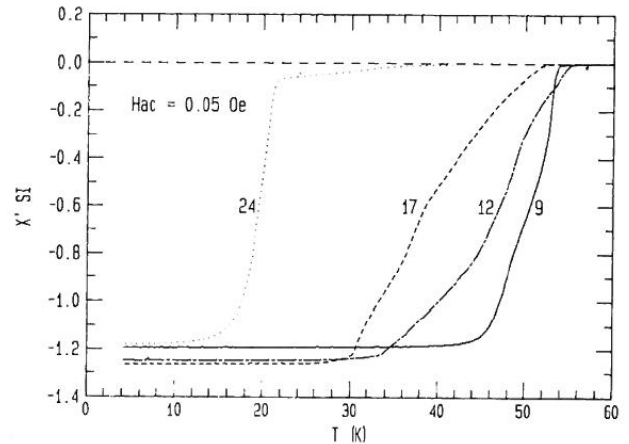


Fig. 10. The superconducting transition temperature by AC susceptibility of tetragonal 2201 after different heat treatments.  $H_{AC}=0.05$  Oe,  $H_{DC}=0$  T. (9) As prepared followed by 2 hours in argon at  $500^\circ C$ . (12)+1 hour in vacuum ( $5 \times 10^{-2}$  atm) at  $475^\circ C$ . (17) Repeated treatment. (24) Subsequent anneal at  $475^\circ C$  in argon. Encapsulated quartz tubes.

temperature of about 6 K and a very low level of superconductivity which was easily destroyed by an external field of 1T. As expected for the tetragonal symmetry [5], the superconducting transition temperature is strongly dependent on the heat treatment (fig. 10) which affects both the oxygen content and the thallium stoichiometry. The tetragonal sample used for the measurements reported in fig. 10 was obtained after the heat treatments I + II (see table 2) and was initially not superconducting down to 4.2 K. Annealing in argon for 2 h at  $500^\circ C$  resulted in a weight loss of 0.1%. This is thought to be due to oxygen departure.  $T_c$  grew to 53 K (number 9 in fig. 10)

corresponding to the compound  $Tl_{1.83}Ba_2CuO_{5.693}$  assuming  $O = 6$  initially. Further annealing in vacuum ( $5 \times 10^{-2}$  atm) at  $475^\circ C$  decreased the Tl content to 1.77 without change of  $T_{c \text{ onset}}$ , but here the large transition reflects a composition gradient in the samples (numbers 12 and 17 in fig. 10). Subsequent treatment in an encapsulated silica tube under argon pressure allowed the equilibrium to be established for  $Tl_{1.77}Ba_2CuO_{5.603}$  with a critical temperature of  $T_c=22$  K (number 24 in fig. 10).

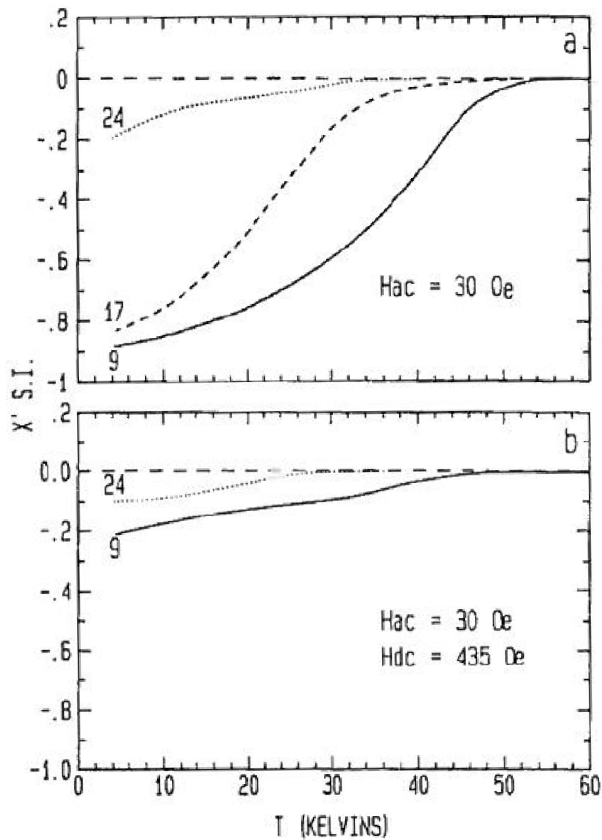


Fig. 11. AC susceptibility of samples of fig. 10 but under a strong AC field (30 Oe). A superimposed DC field is supposed to reveal the grain contribution but here is interfered with the grain size of our samples, less than the penetration depth.

It is worth noting that despite the large screening level ( $\chi = -1$  SI), the grain contribution revealed by the effect of a superimposed DC field on a strong AC field (30 Oe) is of the order of 10% volume (fig. 11), largely lower than the percolation threshold. This apparent contradiction may result from the grain size of our samples, a few 1000 Å, less than the penetration

depth. Metallographic observations support this assumption.

In conclusion we have established a working method to prepare orthorhombic  $Tl_2Ba_2CuO_6$ , excluding the formation of  $BaCuO_2$ . At normal pressure, the transition from orthorhombic to tetragonal "2201" implies thallium deficiency and was found to be inversible. Superconductivity could not be found on samples with the orthorhombic-type structure which, however, displayed a magnetic-like ordering at low temperature.

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