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Single Crystal Study of the 'BaSr' 1212 Superconductor $Tl_{1+x}BaSrCa_{1-x}Cu_2O_{7-\delta}$

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Abstract

Single crystals of the 'BaSr' thallium cuprate $Tl_{1+x}BaSrCa_{1-x}Cu_2O_{7-\delta}$ have been grown for the first time. The structure parameters of this tetragonal phase were successively refined using four single-crystal X-ray diffraction data of the same crystal, as-grown [$T_c = 62$ K, $a = 3.8271$ (7), $c = 12.385$ (3) Å] and after different thermal treatments: two annealings under H_2/Ar flow [$T_c = 90$ K, $a = 3.8356$ (7), $c = 12.390$ (3) Å] and one under oxygen pressure $P_{O_2} = 100$ bar [$T_c = 60$ K, $a = 3.8234$ (9), $c = 12.384$ (4) Å]. The corresponding results provided evidence of a reversible evolution of the cation oxygen distances and of the thallium splitting depending on the reducing/oxidizing conditions of annealing which are well correlated to the superconducting properties. A relationship between T_c's of this $Tl_{1.22}Ba_{1.04}Sr_{0.96}Ca_{0.78}Cu_2O_{7-\delta}$ 'BaSr' 1212 crystal and Cu—Cu distances is compared with the results obtained for pure 'Ba' and 'Sr' 1212 phases.

Introduction

Numerous investigations have been performed on the layered thallium cuprates owing to their critical temperature (T_c) which covers a wide range up to 130 K. Their high sensitivity to the nature of the annealing atmosphere at low temperature (Hervieu *et al.*, 1988; Shimakawa *et al.*, 1989; Martin *et al.*, 1990; Morosin, Baughman, Ginley, Schirber & Venturini, 1990) has shown that the hole carrier density is a predominant factor in the optimization of the critical temperature of these materials. Although the influence of oxygen non-stoichiometry upon T_c's is well established, the relationships between the structure, chemical bonding and superconductivity is so far not understood. This is, for instance, the case with the thallium 1212-cuprates $Tl_{1+x}Ba_2Ca_{1-x}Cu_2O_{7-\delta}$ (Morosin *et al.*, 1988; Morosin, Baughman, Ginley, Schirber & Venturini, 1990) and $Tl_{1+x}Sr_2Ca_{1-x}Cu_2O_{7-\delta}$ (Izumi *et al.*, 1991) that exhibit very different T_c's of 103 (Morosin *et al.*, 1988) and 58 K (Izumi *et al.*, 1991), respectively, in spite of their very similar chemical composition, $x = 0.17$–0.12 and $\delta = 0.25$–0.22. This would imply mean oxidation states of copper of 2.16 and 2.24 for the Ba and Sr phases, respectively, suggesting that the latter is overdoped with respect to the barium cuprate. Nevertheless, all attempts to increase the T_c's of the Sr phase by annealing in reducing conditions did not allow a T_c higher than 68 K to be obtained (Kubo, Kondo, Shimakawa, Manako & Igarashi, 1992). In order to understand this behaviour, mixed 'BaSr' 1212 cuprates were recently synthesized with critical temperatures ranging from 20 to 100 K (Maignan *et al.*, 1993). There is no doubt that to get the clue to such an issue, accurate crystal data about structure, composition and superconducting properties have to be accumulated. We report here on the structure of a unique single crystal of the mixed-phase $Tl_{1+x}BaSrCa_{1-x}Cu_2O_{7-\delta}$, submitted to different thermal treatments in H_2–Ar flow and under oxygen pressure. This investigation is completed by a magnetic study of a crystal of similar parameters, with the same cationic composition.

Experimental

The preparation of '1212' crystals was similar to that previously reported (Martin *et al.*, 1993) for the '1223' $Tl(Ba,Sr)_2Ca_2Cu_3O_9$ crystals. Appropriate

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amounts of SrO_2, BaO_2, CaO and CuO corresponding to '$SrBaCaCu_2O_6$' were first mixed and calcined at 1173 K for 12 h. In order to reach the formula $TlBaSrCaCu_2O_{7-\delta}$ the required amount of Tl_2O_3 was then added to the precursor. The powder was then placed in an alumina crucible and sealed in an evacuated quartz tube. This tube was placed in a vertical furnace, heated at 1273 K and then slowly cooled down to 873 K in 180 h. Finally most of the crystals extracted from the batch were identified as Tl 1212 samples, as measured from their Weissenberg photographs. Two crystals were then selected for the X-ray diffraction study and magnetic characterization.

Both samples were studied before and after successive annealings. The reducing annealings were performed at 523 K in an H_2–Ar (10:90) flow and the oxidizing annealings at 673 K under 100 bar of oxygen pressure.

A small crystal (001) plate with dimensions 50 × 59 × 12.5 μm was selected for this study. Four sets of data were registered successively on a CAD-4 diffractometer for this unique crystal corresponding to the as-synthesized grown crystal (as-G), to the same crystal after annealing in an H_2–Ar flow for 30 (an-HA1) and 60 min (an-HA2), and finally annealed under an oxygen pressure of 100 bar for 12 h (an-O3). The crystal glued on a Lindemann fiberglass was unstuck after each registration, submitted to the appropriate thermal treatment and stuck again. Before each registration on the single crystal diffractometer, the quality of the crystal was checked by recording reflexions with a Weissenberg camera. The experimental conditions are summarized in Table 1.

The eight equivalent regions ($h\pm$, $k\pm$, $l+$) of the reciprocal space were systematically registered. These results prove the importance of the absorption correction and confirm the tetragonal symmetry of the crystal (Table 2). The strategy used for the four refinements was identical. One of the equivalent crystallographic spaces was chosen arbitrarily ($h \geq k$, $k > 0$, $l > 0$). Note that the total number of scanned reflections [$I \geq 3\sigma(I)$], as well as the number of independent reflections decreases from the first to the last registration (Table 2).

For the study of the magnetic properties, a single crystal with the dimensions 308 × 296 × 129 μm was selected. Its cell parameters, checked by X-ray diffraction (XRD), are identical to those of the crystal used for the XRD study. This crystal and the crystal for the XRD study were systematically submitted to identical thermal treatments. After each treatment the magnetic properties of the first crystal were investigated in the temperature range 5–110 K using a SQUID magnetometer. The crystal was zero-field cooled and the magnetization *versus* temperature was registered under a field of 10 G.

Table 1. *Crystallographic data*

Formula	$Tl_{1.22}Ba_{1.04}Sr_{0.96}Ca_{0.78}Cu_2O_{7-\delta}$
Formula weight	746.6
Crystal system, space group	Tetragonal, *P4/mmm* (No. 123)
Calculated density, Z*	6.8, 1
Dimensions of the sample (μm)	50 × 59 × 12.5
Diffractometer	CAD-4 Enraf–Nonius
Radiation, monochromator	Mo $K\alpha$, graphite
Scan mode†	ω–θ/3
2θ range (°)	2–45
Octants	$-7 \leq h \leq +7$, $-7 \leq k \leq +7$, $0 \leq l \leq 24$
μ (cm^{-1})*	467
Absorption correction	Analytical
Transmission factors	0.60–0.18

* For the three refined structures, these values are very close together.

† TYPE = 1 value was chosen after profile study of some reflections in the (ω–θ) plane.

Table 2. *Check of the tetragonal symmetry*

Sample	as-G	an-HA1	an-HA2	an-O3
No. of scanned reflections	3063	3063	3069	3043
Total No. of reflections with $I > 3\sigma(I)$	1023	983	981	928
No. of independent reflections	200	187	181	177
$R_{int}(I)$ before absorption corrections	0.083	0.083	0.102	0.096
$R_{int}(I)$ after absorption corrections	0.030	0.032	0.031	0.036

Results and discussion

The structure determinations performed in the space group *P4/mmm* show that all the heavy atoms are located in a unique site, except thallium which is distributed over the (x,0,0) split sites with an occupancy factor of 1/4. No thallium deficiency is observed in the $[TlO]_\infty$ sheet. The positions of the three independent O atoms, deduced from the difference series, show unique sites. In particular, no splitting is observed for the O(3) position corresponding to the $[TlO]_\infty$ layer, in agreement with the results obtained for the 1212 strontium and barium cuprates (Izumi *et al.*, 1991; Morosin *et al.*, 1988), and contrary to the cuprates $TlBa_2Ca_{1-x}Nd_xCu_2O_{7-\delta}$ (Michel *et al.*, 1991). However, the height of the series difference peaks, ranging from 15 (crystal an-HA1) to 17 e Å^{-3} (crystal an-O3) suggests that this site is almost fully occupied even for the crystal submitted to a reducing atmosphere, contrary to the pure barium and strontium 1212 cuprates. The refinements of the occupancy factor of the calcium sites show that the latter are partially occupied by thallium, moreover the occupancy does not vary with the thermal treatment. In the same way the $2h$ sites are half occupied by barium and half by strontium, whatever the thermal treatment.

The ultimate refinements carried out with *SDP* programs (B. A. Frenz & Associates Inc., 1982), using the anisotropic thermal factors lead to the atomic coordinates listed in Table 3. The corresponding highest residues correspond to 1.5 e Å^{-3}. Note that the atomic coordinates are identical for the

Table 3. *Atomic parameters and R values*

State of the sample		as-G	an-HA1	an-O3
Tl 4*l* (*x*,0,0)*	*x*	0.0859 (6)	0.0949 (5)	0.0862 (6)
	B_{eq}	2.57 (5)	2.45 (4)	1.91 (5)
CT† 1*d* ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$)	B_{eq}	0.83 (2)	1.06 (2)	0.79 (2)
BS‡ 2*h* ($\frac{1}{2},\frac{1}{2},z$)	*z*	0.21450 (9)	0.21615 (9)	0.2128 (1)
	B_{eq}	1.03 (1)	1.12 (1)	0.99 (1)
Cu 2*g* (0,0,*z*)	*z*	0.3685 (1)	0.3698 (1)	0.3675 (2)
	B_{eq}	0.83 (2)	0.96 (2)	0.80 (2)
O(1) 4*i* ($\frac{1}{2}$,0,*z*)	*z*	0.3755 (6)	0.3744 (6)	0.3749 (8)
	B_{eq}	1.4 (1)	1.4 (1)	1.2 (2)
O(2) 2*g* (0,0,*z*)	*z*	0.1629 (9)	0.1621 (8)	0.164 (1)
	B_{eq}	1.8 (1)	1.7 (1)	1.3 (1)
O(3) 1*c* ($\frac{1}{2},\frac{1}{2}$,0)	B_{eq}	3.3 (3)	3.1 (3)	2.2 (3)
R		0.025	0.024	0.028
wR		0.025	0.024	0.031
Goodness of fit		1.315	1.279	1.737

* Shifted from 1*a* (0,0,0)
† CT = 0.78 (1) Ca + 0.22 (1) Tl.
‡ BS = 0.52 (2) Ba + 0.48 (2) Sr.

[an-HA1] and [an-HA2] crystals; clearly this proves that the first H_2–Ar annealing is efficient and that the reduction does not continue during the second annealing. Only the [an-HA1] results are given in Table 3.

These structural refinements show that the chemical composition of the crystal is well represented by the formula $Tl_{1.22}Ba_{1.04}Sr_{0.96}Ca_{0.78}Cu_2O_{7-\delta}$. The analysis of these results allows the following features to be evidenced for this 1212 structure (Fig. 1).

(i) The great ability of thallium to occupy the calcium sites is confirmed. This is the highest occupancy rate with 22% on the Ca site of the Tl 1212-based cuprates that has been observed up to now, to be compared with 17% for $Tl_{1.17}Ba_2Ca_{0.83}Cu_2O_{6.75}$ (Morosin *et al.*, 1988) and 12% for $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{7-\delta}$ (Izumi *et al.*, 1991). This excess thallium may be necessary to stabilize the 1212 structure by bringing additional oxygen with respect to the corresponding molar ratio Tl/(Sr,Ba) = 1/2: the ideal compound $TlBaSrCaCu_2O_7$ would indeed require too high a mean oxidation state of copper to be synthesized under an oxygen pressure of a few bars.

(ii) The refined atomic coordinates are not strongly affected by the thermal treatments. The (*z*) parameters of Cu and BaSr atoms tend to decrease as the oxygen content is increased.

(iii) The most important feature deals with the occupancy factor of the O(3) site of the $[TlO]_\infty$ layers, which was refined to 1 whatever the thermal treatment. This behaviour is different from that of the pure barium and pure strontium cuprates, of which rather high δ values of 0.25 (Morosin *et al.*, 1988) and 0.22–0.12 (Izumi *et al.*, 1991) were found, respectively. Note, however, that the rather high *B*[O(3)] values of 3.3–3.1 Å^2 observed for the [as-G] and [an-HA] crystals suggest the presence of oxygen vacancies, whereas the decrease of *B*[O(3)] down to 2.2 for the [an-O3] crystal indicates that the rate of oxygen vacancies has decreased by annealing the crystal under an oxygen pressure of 100 bar. In any case, the amount of oxygen vacancies in the $[TlO]_\infty$ layer remains too small to be directly detected by our X-ray analysis, in agreement with the small value found by neutron studies on the pure strontium phase $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{7-\delta}$ $(0.12 \leq \delta \leq 0.22)$ which showed a 10% oxygen content variation between its [as-G] and [an-Ar] samples. Moreover, the variation of the splitting of the thallium sites is significantly influenced by argon annealing, as observed from the latter study $(0.0724 < x_{Tl} < 0.0798)$ and from our results $(0.0859 < x_{Tl} < 0.0949)$. This suggests that the amplitude of the splitting is sensitive to a small variation of the amount of oxygen vacancies in the $[TlO]_\infty$ layers. Nevertheless, it is not known whether the displacement of thallium from its ideal position (0,0,0) is only due the presence of these oxygen vacancies.

The evolution of the cell parameters and of the interatomic distances compared with those of $Tl_{1.17}Ba_2Ca_{0.83}Cu_2O_{6.75}$ (Morosin *et al.*, 1988) and $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{6.78}$ (Izumi *et al.*, 1991) is shown in Table 4. Note that in the study of the 'Ba' 1212,

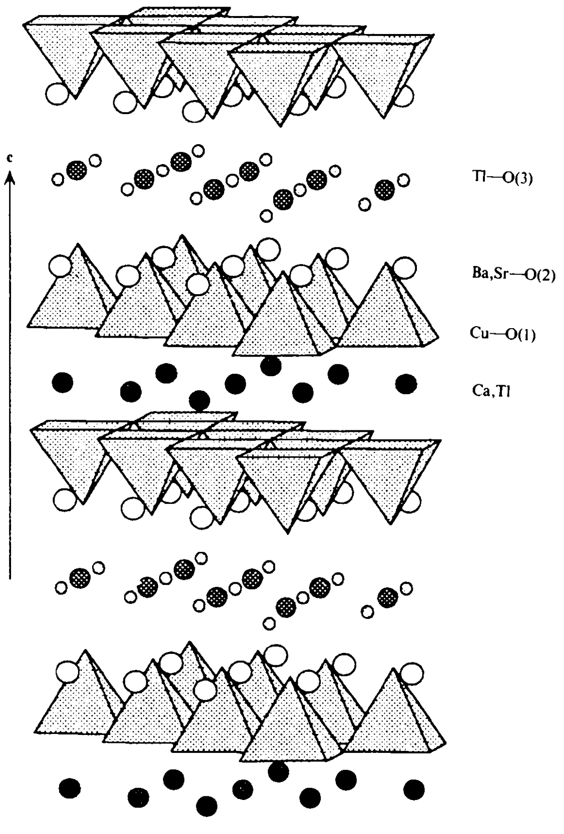

Fig. 1. Schematic structure of the '1212'-type superconductor $Tl_{1+x}BaSrCa_{1-x}Cu_2O_7$.

Table 4. *Cell parameters and interatomic distances* (Å)

	as-G	an-HA1	an-O3	'Ba' as-G*	'Sr' as-G	'Sr' an-AR
a	3.8271 (7)	3.8356 (7)	3.8234 (9)	3.8566 (4)	3.78135 (6)	3.79207 (7)
c	12.385 (3)	12.390 (3)	12.384 (4)	12.754 (2)	12.1087 2)	12.1178 (2)
V (Å^3)	181.6	182.3	181.0	189.7	173.1	174.2
c/a	3.2388	3.2301	3.2389	3.3075	3.2022	3.1955
Tl—O(2)	2.05 (1)	2.04 (1)	2.06 (1)	2.06 (2)	2.042 (3)	2.033 (3)
Tl—O(3)	2.484 (2)	2.468 (2)	2.481 (2)	2.450 (3)	2.488 (4)	2.477 (3)
Tl—O(3)	2.948 (2)	2.981 (2)	2.946 (2)	3.036 (3)	2.874 (4)	2.903 (4)
CT—O(1)†	2.458 (4)	2.469 (4)	2.460 (5)	2.470 (7)	2.453 (1)	2.461 (1)
BS—O(1)‡	2.765 (5)	2.743 (5)	2.773 (6)	2.837 (8)	2.694 (2)	2.662 (2)
BS—O(2)	2.781 (2)	2.794 (2)	2.770 (2)	2.825 (5)	2.7295 (7)	2.7502 (7)
BS—O(3)	2.659 (1)	2.678 (1)	2.635 (1)	2.752 (2)	2.572 (2)	2.622 (2)
Cu—O(1)	1.9155 (3)	1.9186 (2)	1.9139 (4)	1.929 (1)	1.8940 (2)	1.8979 (1)
Cu—O(2)	2.55 (1)	2.57 (1)	2.52 (1)	2.76 (2)	2.355 (4)	2.396 (4)
CuO(2)/CuO(1)	1.331	1.339	1.317	1.430	1.243	1.262
Cu—Cu	3.260 (3)	3.226 (4)	3.282 (4)	3.201	3.352	3.305

* Only Tl_D—O and Ba—O distances appear in this column. Note: Tl—O(2) = 2.01 (4), Tl—O(3) = 2.727 (1) Å (undisplaced Tl) and Ba_D—O(1) = 3.36 (4), Ba_D—O(2) = 2.728 (2), Ba_D—O(3) = 2.08 (4) Å (displaced Ba).

† CT = 0.78 (1) Ca + 0.22 (1) Tl.

‡ BS = 0.52 (2) Ba + 0.48 (2) Sr.

both thallium and barium occupy two sites, the 'ideal' positions (0,0,1/2) and (1/2,1/2,0.2842) and the displaced sites (0.108,0,1/2) and (1/2,1/2,0.337). In Table 4, Tl_D–O and Ba_D–O correspond to the displaced atoms. One observes that the *a* and *c* parameters of the 'BaSr' phases are intermediate between those of the 'Ba' and 'Sr' phases. In a similar way, the Ba(Sr)—O distances are intermediate between the Sr—O distances of the 'Sr' phase and the Ba—O distances of the 'Ba' phase (in agreement with the size of these two cations). It is remarkable that the replacement of strontium by barium induces a significant increase of the Cu—O distances, as shown from all the Cu—O bonds of this 'BaSr' crystal that are intermediate between those of the pure 'Ba' and pure 'Sr' 1212 cuprates. The latter effect is particularly important on the Cu—O apical bonds of the CuO_5 pyramids (2.52–2.57 Å for 'BaSr' against 2.76 Å for 'Ba' and 2.35–2.39 Å for 'Sr'). As in the other thallium cuprates, thallium exhibits a tetrahedral coordination with very similar Tl—O distances. In fact, the tetragonal symmetry observed for all these cuprates implies an average structure due only to the displacement of the Tl atom from its ideal position inside its oxygen octahedron. Taking into consideration the absence of diffusion streaks on the XRD patterns, this feature characteristic of all thallium cuprates can be explained by a random distribution of Tl over all the off-centred split positions; this leads by an average effect to the *P*4/*mmm* symmetry, each octahedron being on average occupied by one Tl atom.

A remarkable feature deals with the evolution of all the cation–oxygen distances with the annealing treatment, in agreement with Izumi *et al.* (1991). One indeed observes that the equatorial Cu—O distances decrease from 1.9186 (2) to 1.9139 (4) Å and the Cu—O apical distances from 2.57 (1) to 2.52 (1) Å (Table 4) as the oxygen content increases. This decrease of the size of the CuO_5 pyramid is in agreement with an increase of the Cu^{III} content, *i.e.* of the hole carrier density as the oxygen content increases. This evolution can be correlated to the superconducting properties of the crystal with an identical cationic composition and submitted to identical treatments (Fig. 2). One observes that the T_c's increase in a continuous manner from 50 K for the overdoped [an-O3] crystal to 62 K for the [as-G] still overdoped crystal, to 90 K for the [an-HA] crystal that exhibits the largest Cu—O bonds and is consequently less doped. The effect is similar for the pure Sr-cuprate (Table 4) which shows a T_c of 58 K for the argon-annealed sample that exhibits larger CuO_5 pyramids, whereas the as-synthesized sample which is overdoped does not superconduct. Never-

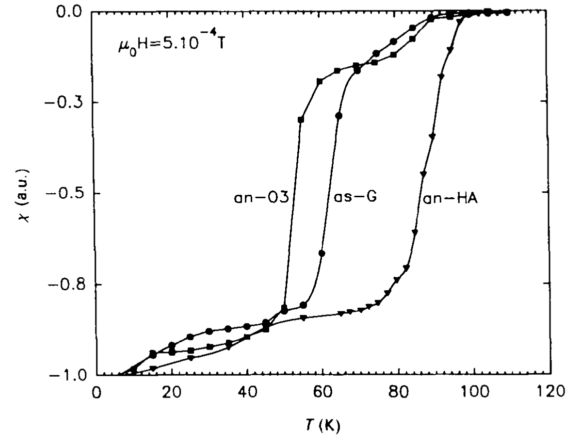

Fig. 2. Temperature dependence of the susceptibility $\chi(T)$ for the $Tl_{1+x}BaSrCa_{1-x}Cu_2O_7$ crystal registered after zero-field cooling at 5 K. As grown (as-G), annealed in H_2–Ar flow (an-HA) and then annealed under oxygen pressure (an-O3).

theless, it must be emphasized that the T_c's cannot be correlated in any case to the absolute value of the Cu—O distance: for instance, the two phases [as-G] $Tl_{1.22}BaSrCa_{0.78}Cu_2O_{7-\delta}$ and $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{6.78}$ exhibit close T_c values of 62 and 58 K, respectively, but very different apical Cu—O bonds of 2.55 and 2.39 Å, respectively.

It is worth pointing out that these phenomena are reversible: by annealing the [an-HA] sample under an oxygen pressure of 100 bar T_c decreases again and correlatively the splitting of Tl decreases very close to the initial value (Table 3). The most important result of this study deals with the evolution of the Cu–Cu interlayer distance between the two pyramidal copper layers, with thermal treatment. The continuous increase of the Cu—Cu distance (Table 4) from 3.226 to 3.282 Å, and correlatively the decrease of the T_c's from 90 to 50 K, as the oxygen content increases is remarkable. This behaviour can be extended to the pure 'Ba' and 'Sr' compounds: the Ba-cuprate $Tl_{1.17}Ba_2Ca_{0.83}Cu_2O_{6.75}$ that exhibits the highest T_c's of all the series (103 K) exhibits the smallest Cu—Cu distance (3.20 Å), whereas the Sr-phase $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{6.88}$ that does not superconduct is characterized by the largest Cu—Cu distance (3.35 Å). One observes a linear evolution of the Cu–Cu distance *versus* T_c for five cuprates (Fig. 3). Nevertheless, the superconducting phase $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{6.78}$ that exhibits a T_c of 58 K with a Cu–Cu distance of 3.305 Å does not fit correctly with this evolution.

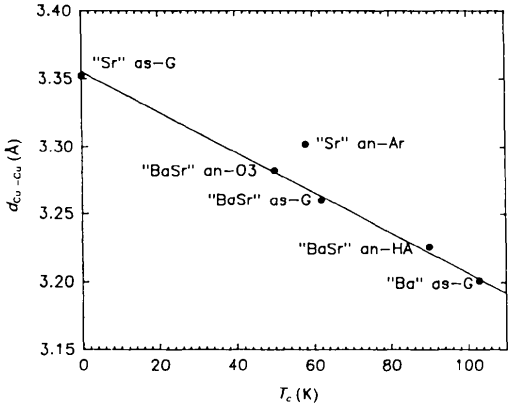

Fig. 3. Cu–Cu distances *versus* T_c for the different 1212 phases: our $Tl_{1.22}BaSrCa_{0.78}Cu_2O_{7-\delta}$ abbreviated 'BaSr' as-grown (as-G) and after the different thermal treatments (an-HA and an-O_3), $Tl_{1.12}Sr_2Ca_{0.88}Cu_2O_{7-\delta}$ abbreviated 'Sr' as-grown (as-G) and after an annealing under argon flow (an-Ar), $Tl_{1.17}Ba_2$-$Ca_{0.83}Cu_2O_{7-\delta}$ abbreviated 'Ba' as-grown (as-G).

Concluding remarks

This study has allowed correlations between the critical temperature and the accurate structures of a same single crystal submitted to various thermal treatments to be established. The systematic measurements of the Seebeck coefficient of that crystal will be performed to understand the relationships between the hole carrier density, the structural data and T_c's.

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