

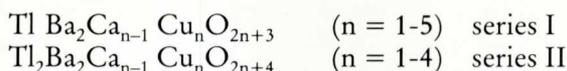
# THE STRUCTURES OF Tl-SUPERCONDUCTING SINGLE CRYSTALS

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In this paper we report results of structure determinations carried out at the Laboratory of X-ray Structure Analysis of the Institute of Crystallography, USSR Acad. Sci., under the State Program of HTSC Investigations. In recent 3 years we have been working in collaboration with various groups of other Academy's Institutes, such as Institute of Physics, Institute of Solid State Physics, Institute of Chemical Physics. Due to these close contacts we have obtained high-quality single crystals for structure determinations; main results have been published elsewhere [1-4]. This communication reports X-ray diffraction studies of only Tl-containing superconducting materials and specific structural features of some thallium cuprates.

All the diversity of Tl-containing superconductors can be conditionally divided into two series of phases:



The 2223 phase of the second series is characterized by the highest superconducting transition temperature, 125K. The main difference between these two series is as follows: all the phases of the 1st series contain a single layer of Tl-octahedra, while the second one contains a double layer of such octahedra linked according to the rock-salt motif. The phases within each series differ in the number of Cu-O sheets located in the perovskite block of the structure.

Superconductivity in Tl-cuprates is believed to originate from the presence of holes in  $\text{CuO}_2$ -planes, while TlO-layers serve as reservoir of charge carriers. In the case of strict stoichiometry a formal oxidation state of Cu in the 1st series varies from  $\text{Cu}^{3+}$  to  $\text{Cu}^{2.2+}$  upon n changing from 1 to 5. In the 2nd series all the copper atoms have the formal oxidation state 2 exactly. It

is known, however, that a compound becomes a superconductor when some copper atoms are oxidized up to 3+, so as holes arise. That is why cationic vacancies and replacements of any kind which are not of major importance for single-Tl-layer cuprates (except the 1st member with  $n=1$ ) are vital for the whole family of cuprates with double Tl-layers.

Various authors give different estimations about the presence of vacancies, isomorphous replacements, atomic shifts in cationic and anionic sublattices of Tl-containing superconductors. This study thus affords an attempt to determine the cation and oxygen distributions which may be dependent on the growing technique and conditions.

Preparation of HTSC samples suitable for X-ray structure analysis is a kind of art. Our colleagues from the Institute of Solid State Physics put their efforts in preparing samples with the highest possible  $T_c$  for the given phase under certain preparation conditions. As a result, we have got samples of four different phases grown from solution in melt in oxygen flux under normal pressure;  $T_c$  was found from the temperature dependence of the magnetic moment (Table 1). Three phases were superconductors.

Table 1. Composition and  $T_c$  for the crystals.

| abbreviation | crystal composition  |   | $T_c$ , K   |
|--------------|--|---|---|
| 2201         | ( Tl <sub>0.92</sub> <sup>3+</sup> Cu <sub>0.08</sub> <sup>1+</sup> ) <sub>2</sub> Ba <sub>2</sub> |   | Cu <sup>2.32+</sup> O <sub>6</sub> 112              |
| 2212         | ( Tl <sub>0.93</sub> <sup>3+</sup> Cu <sub>0.07</sub> <sup>1+</sup> ) <sub>2</sub> Ba <sub>2</sub> | Ca <sub>0.90</sub> <sup>2+</sup> Tl <sub>0.10</sub> <sup>3+</sup> | Cu <sub>2</sub> <sup>2.09+</sup> O <sub>8</sub> 110 |
| Ca-1212      | Tl Ba <sub>2</sub>   | Ca <sub>0.87</sub> <sup>2+</sup> Tl <sub>0.13</sub> <sup>3+</sup> | Cu <sub>2</sub> <sup>2.44+</sup> O <sub>7</sub> 80  |
| La-1212      | Tl Ba <sub>2</sub>   | La <sup>3+</sup>  | Cu <sub>2</sub> <sup>2.00+</sup> O <sub>7</sub> -   |

The lanthanum analogue of the 1212 phase did not undergo a superconducting phase transition. The samples selected for the experiment were thin plates except the 2212 phase. A plate of 2212 phase was thick, that is why we prepared a rounded sample to make absorption correction more simple.

Single crystal diffraction data were taken at room temperature on an ENRAF-NONIUS CAD4F diffractometer using  $AgK_{\alpha}$ -radiation. All the samples were preliminarily tested for absence of epitaxial phases, absence of twinning, absence of satellite reflections and reflections violating space groups P4/mmm (1st series) or I4/mmm (2nd series). In our tests we mainly used two-dimensional angular scanning of the chosen areas of reciprocal space [2].

The data were collected in five octants of reciprocal space with the radius of 0.8-1.1  $\text{\AA}^{-1}$ , background measurements were optimized for weak reflections. Before averaging symmetry equivalent reflections, absorption correction was applied by numerical integration with an account of the crystal shape (Table 2). The structural models were refined according to the local PC-version of the PROMETHEUS program package [5].

Table 2. Summary of crystallographic information for 2201, 2212, Ca-1212 and La-1212 crystals

|                          | 2201       | 2212       | Ca-1212    | La-1212    |
|--------------------------|------------|------------|------------|------------|
| Sample size, mm          | 0.90-0.3   | $r=0.113$  | 0.04-0.25  | 0.04-0.39  |
| Space group              | I4/mmm     | I4/mmm     | P4/mmm     | P4/mmm     |
| a, $\text{\AA}$          | 3.869 (1)  | 3.852 (3)  | 3.847 (1)  | 3.944 (1)  |
| c, $\text{\AA}$          | 23.259 (5) | 29.290 (6) | 12.721 (3) | 12.607 (3) |
| V, $\text{\AA}^3$        | 348.17 (2) | 434.60 (2) | 188.26 (2) | 196.10 (2) |
| $\mu$ , $\text{cm}^{-1}$ | 333.9      | 279.2      | 206.5      | 220.1      |
| Measured reflections     | 2824       | 2358       | 2509       | 4097       |
| Independent reflections  | 313        | 239        | 284        | 674        |
| $R(I)_{\text{aver}}$ , % | 4.7        | 6.5        | 9.6        | 5.9        |
| $R/R_w$ , %              | 1.40/1.62  | 1.67/1.62  | 3.40/3.20  | 1.58/2.08  |

In the refinements we paid special attention to the strongly correlating parameters of the structural models, in particular, to occupancy coefficients, thermal parameters and slight shifts of Tl and O atoms. In some cases we used step-by-step scanning of the correlating parameters [6]. Besides R-factor we considered difference electron density maps as a criterion. The results of our studies are listed in Tables 3-7.

The R-factors (Table 2) evidence a rather high reliability of the obtained data. None of the structures showed oxygen site deficiency. Note that Tl atoms occupy Ca sites in the Ca-containing phases in similar amounts. Cu atoms also occupy Tl sites in similar percentage. Apparently, this situation is due to preparation conditions and explains the fact that different papers report different values for samples obtained at other laboratories.

In all our studies we observed disordering effects only in Tl-O layers (Figures 1-2). Oxygen atom displacement in double-Tl-layer phases is reported by many authors. We have also observed Tl-atom displacement from symmetry sites. This displacement is less significant than that of O atoms but it occurs in the same ab-diagonal direction and is characteristic both of the 2212 and 2201 phases.

**Table 3. Positional and thermal parameters for the atoms of Ca-1212 structure (for details see ref. 3)**

| Atom          | Occupancy        | x          | y   | z           | B <sub>eq.</sub> |
|---------------|------------------|------------|-----|-------------|------------------|
| Tl            | 1.0              | 0.0877 (4) | 0.0 | 0.0         | 1.76 (4)         |
| Ba            | 1.0              | 0.5        | 0.5 | 0.21550 (5) | 0.55 (2)         |
| Cu            | 1.0              | 0.0        | 0.0 | 0.3740 (1)  | 0.44 (2)         |
| Ca<br>+<br>Tl | 0.87 (1)<br>0.13 | 0.5        | 0.5 | 0.5         | 0.47 (4)         |
| 01            | 1.0              | 0.5        | 0.0 | 0.3797 (5)  | 0.7 (1)          |
| 02            | 1.0              | 0.0        | 0.0 | 0.1582 (7)  | 1.1 (1)          |
| 03            | 1.0              | 0.5        | 0.5 | 0.0         | 2.6 (3)          |

**Table 4. Positional and thermal parameters for the atoms of La-1212 structure**

| Atom | Occupancy | x          | y   | x           | B <sub>eq.</sub> |
|------|-----------|------------|-----|-------------|------------------|
| Tl   | 1.0       | 0.0755 (1) | 0.0 | 0.0         | 1.46 (4)         |
| Ba   | 1.0       | 0.5        | 0.5 | 0.20654 (2) | 0.74 (1)         |
| Cu   | 1.0       | 0.0        | 0.0 | 0.35922 (5) | 0.68 (1)         |
| La   | 1.0       | 0.5        | 0.5 | 0.5         | 0.70 (1)         |
| 01   | 1.0       | 0.5        | 0.0 | 0.3733 (2)  | 0.88 (2)         |
| 02   | 1.0       | 0.0        | 0.0 | 0.1648 (4)  | 1.7 (1)          |
| 03   | 1.0       | 0.626      | 0.5 | 0.0         | 2.0 (2)          |

**Table 5. Positional and thermal parameters for the atoms of 2201 structure**

| Atom            | Occupancy               | x          | y          | z          | B <sub>eq.</sub> |
|-----------------|-------------------------|------------|------------|------------|------------------|
| Tl<br>+<br>Cu'  | 0.930 (4)<br>+<br>0.070 | 0.5207 (3) | 0.5207 (3) | 0.2029 (2) | 1.04 (2)         |
| Cu1             | 1.0                     | 0.5        | 0.5        | 0.0        | 0.62 (3)         |
| Ba              | 1.0                     | 0.0        | 0.0        | 0.0833 (2) | 0.73 (2)         |
| 01              | 1.0                     | 0.0        | 0.5        | 0.0        | 0.8 (1)          |
| 02              | 1.0                     | 0.5        | 0.5        | 0.1171 (3) | 1.1 (2)          |
| 0.3<br>+<br>03' | 0.93<br>+<br>0.07       | 0.552 (2)  | 0.552 (2)  | 0.2892 (4) | 2.2 (8)          |
|                 |                         | 0.5        | 0.5        | 0.2749 (7) | 1.3 (4)          |

**Table 6. Positional and thermal parameters for the atoms of 2212 structure (for details see ref. 4)**

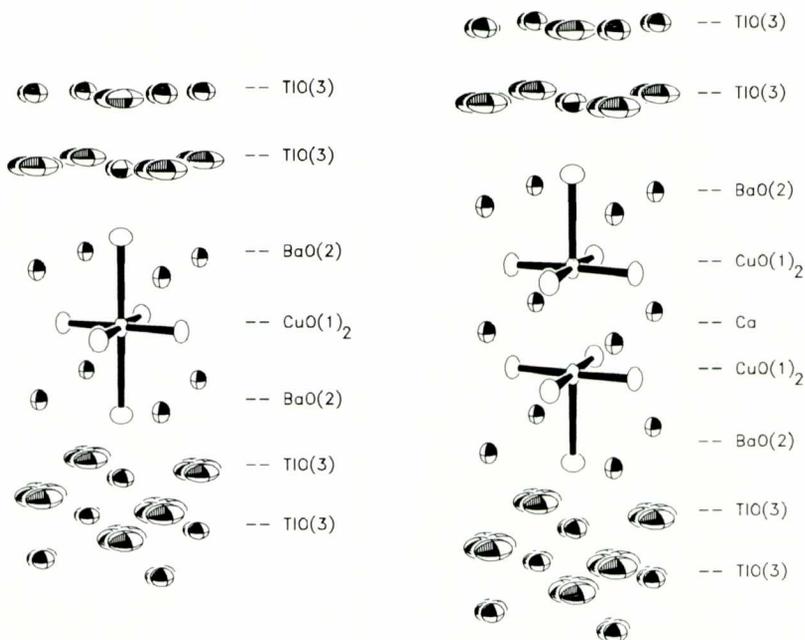
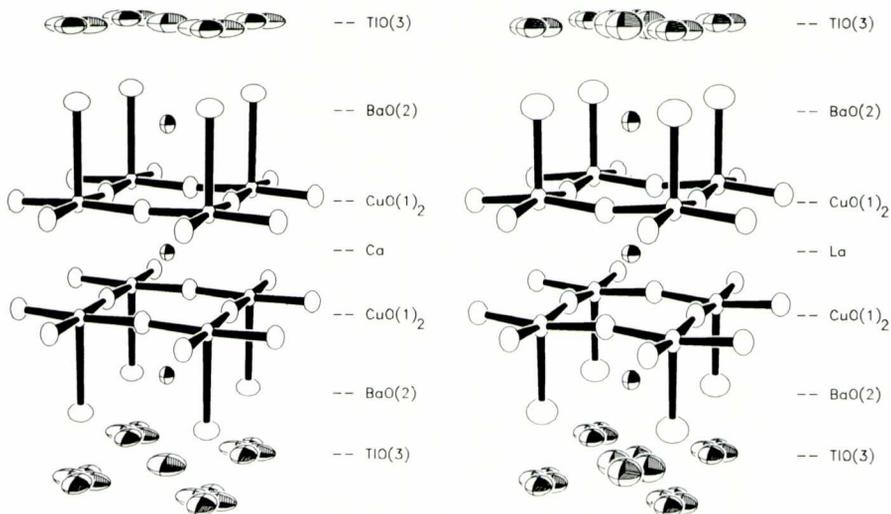
| Atom    | Occupancy      | x          | y          | z           | B <sub>eq.</sub> |
|---------|----------------|------------|------------|-------------|------------------|
| Tl<br>+ | 0.901 (4)<br>+ | 0.5252 (3) | 0.5252 (3) | 0.21368 (2) | 1.00 (2)         |
| Cu'     | 0.099          | 0.5        | 0.5        | 0.20803 (7) | 1.01 (4)         |
| Cu1     | 1.0            | 0.5        | 0.5        | 0.05399 (4) | 0.47 (2)         |
| Ba      | 1.0            | 0.0        | 0.0        | 0.12156 (2) | 0.69 (2)         |
| Ca<br>+ | 0.896 (4)<br>+ | 0.0        | 0.0        | 0.0         | 0.59 (4)         |
| Tl      | 0.104          |            |            |             |                  |
| 01      | 1.0            | 0.0        | 0.5        | 0.0524 (1)  | 0.8 (2)          |
| 02      | 1.0            | 0.5        | 0.5        | 0.1451 (3)  | 1.4 (3)          |
| 03<br>+ | 0.901<br>+     | 0.559 (3)  | 0.559 (3)  | 0.2817 (5)  | 4.0 (7)          |
| 03'     | 0.099          | 0.5        | 0.5        | 0.2709 (8)  | 1.2 (5)          |

**Table 7. Comparison of selected interatomic distances (Å)**

| Bond        | La-1212        | Ca-1212        | 2201            | 2212            |
|-------------|----------------|----------------|-----------------|-----------------|
| Tl-02       | 2.098 (5) (x2) | 2.040 (9) (x2) | 2.030 (8) (x2*) | 2.010 (7) (x2*) |
| -03         | 2.297 (6) (x2) | 2.493 (1) (x2) | 2.445 (1) (x2*) | 2.330 (1) (x2*) |
| -03         | 2.932 (9) (x2) | 2.968 (1) (x2) | 2.889 (1) (x2*) | 2.850 (1) (x2*) |
| Cu-01       | 1.980 (2) (x4) | 1.924 (3) (x4) | 1.920 (2) (x4)  | 1.927 (2) (x4)  |
| -02         | 2.452 (5) (x1) | 2.745 (9) (x1) | 2.725 (8) (x2)  | 2.675 (7) (x1)  |
| Ba-01       | 2.882 (2) (x4) | 2.839 (5) (x4) | 2.727 (3) (x4)  | 2.792 (3) (x4)  |
| -02         | 2.838 (1) (x4) | 2.816 (2) (x4) | 2.827 (2) (x4)  | 2.811 (2) (x4)  |
| -03         | 2.651 (2) (x1) | 2.741 (1) (x1) | 2.980 (2) (x1)  | 2.845 (3) (x1)  |
| Ca/La-01    | 2.538 (2) (x8) | 2.458 (4) (x8) | –               | 2.463 (3) (x8)  |
| Tl shift ** | 0.31           | 0.34           | 0.11            | 0.14            |
| O shift **  | 0.50           | –              | 0.23            | 0.26            |

\*) mean distances for groups of bonds which are equivalent in terms of crystal chemistry are presented here. In the 2201 and 2212 structures Tl-bonds with apical oxygen atoms are regarded as equivalent.

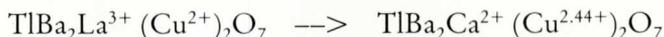
\*\*) displacement of Tl and O atoms from symmetry positions (0, 0, 0), (1/2, 1/2, 0) or (1/2, 1/2, z).



In single-Tl-layer phases Tl atom displacement is usually observed. A typical example is the 1212 phase, containing Ca. But during substitution of Ca for La, oxygen atoms in the Tl-O layer are shifted, too. When  $\text{Ca}^{2+}$  is replaced by  $\text{La}^{3+}$  in the 1212 structure, La atoms are located between  $\text{CuO}_5$  pyramids, setting them apart, Cu-Cu and O-O distances between pyramids become larger, Ba-Ba distances are decreased. If O(3) atoms were at the same place, the distance between these atoms and Ba would be too short, which is not allowed. A natural process to remove steric tensions in the Ba-O(3)-Ba fragment is O(3) atom shifting and disordering, when Ba-O(3) distances are equal to 2.651 Å.

Other changes in the 1212-structure are as follows: upon Ca replacement by La, the c-axis is, on the whole, smaller, due to a significant shortening of the distance between Cu and the apical oxygen atom. Copper atoms are displaced from O planes of the pyramid base. Changes in oxygen coordination of copper evidence variation in its electronic state from 2.44+ to 2+ in terms of formal oxidation state.

A similar disorder is observed in single-Tl-phase 1201, when both O and Tl atoms are shifted from symmetry positions [7]. An example of this phase shows that the crystal can become a superconductor not only when Cu is oxidized from 2+ to 2.44+, as in the 1212 phase upon  $\text{La}^{3+}$  replacement by  $\text{Ca}^{2+}$ :



Reduction of Cu from 3+ to 2.2+ in the 1201 phase upon partial replacement of  $\text{Ba}^{2+}$  by  $\text{La}^{3+}$  is also acceptable:



These two examples show that the effective oxidation state for Cu should be between 2+ and 3+ if this parameter is used as a criterion of the superconducting phase. Moreover, the optimum oxidation state leading to the maximum possible  $T_c$  for the given phase essentially depends on the structure of this phase.

In double-Tl-layer phases the effective oxidation state is only 2.09-2.32, provided our model with partial  $\text{Tl}^{3+}$  replacement by  $\text{Cu}^{1+}$  is correct.

According to structure determinations, the process of disorder involves only those Tl and O atoms that are located in the same layer, because O atoms adjacent to these layers are fixed by large Ba atoms. The sum of ionic radii of  $\text{Tl}^{3+}$  and  $\text{O}^{2-}$  is 2.29 Å [8], the doubled value is 4.58 Å. The length of the vertical "axis" of the Tl-octahedra in 1212, 2212 and 2201 structures is only 4.00-4.02 Å, in the ab-plane it is 5.41-5.48 Å. Therefore, if Tl and/or O

were not shifted, the distances between Tl and apical oxygen atoms would be too short, while those between Tl and equatorial O atoms would be too long. In other words, an octahedra void due to other structural elements is inconvenient for Tl. Atomic disorder in the Tl-O layer can be regarded as an attempt to make a more suitable environment for Tl.

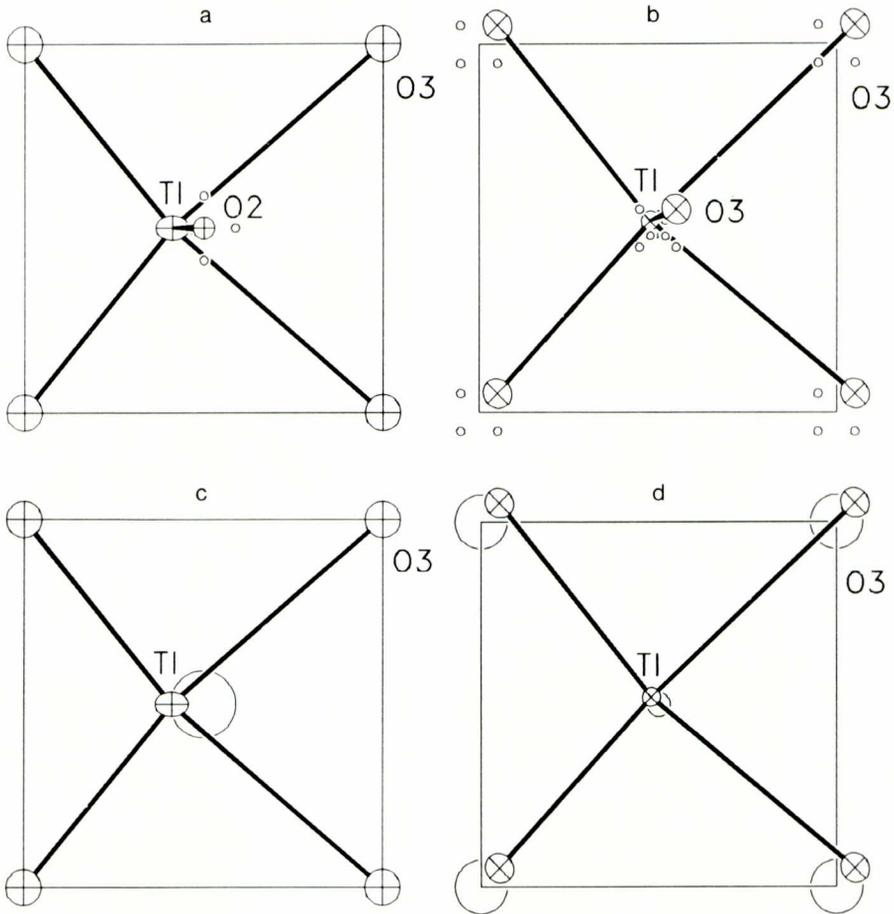


Fig. 3. Projection of Tl-arrangement on the ab-plane:

- a,c – in single-Tl-layer structures,
- b,d – in double-Tl-layer structures.

Only one of four possible positions of Tl and O3 atoms at each site are shown in a and b as crossed circles. Other possible positions are shown as small open circles, Tl-O bonds are also shown. "Circle motion" models for both types of structures are presented on projections c and d.

It was shown in [9], in the pair-distribution-function analysis of pulsed neutron scattering data, that in the 2212 phase there is a correlation between shifted Tl atoms. In [10] a similar conclusion was made on the basis of electron diffraction data for the 2201 phase. Our experience in studies of nonstoichiometric phases also shows that when atoms statistically occupy their sites, this occupation is not independent [11]. As a rule, crystal chemistry regularities are observed locally. In this case correlated shifts of Tl and O atoms may lead to the lowering of symmetry from tetragonal to orthorhombic. Because of short range ordering, X-ray diffraction patterns retain average tetragonal symmetry and do not show any incommensurate modulation like Bi-containing materials, or twinning, like Y- and La-containing superconducting phases.

As stated above, all the structures studied by us exhibit Tl and/or O atom disorder in TlO layers. In this case the distortion of a Tl octahedron changes from 2-4 to 2-2-2. Figure 3 shows some possible configurations of oxygen environment of Tl projected onto the *ab* plane. The configuration which is as close as possible to the only configuration of 1212 was chosen for 2201 and 2212 structures. Table 7 presents mean distances for these particular configurations.

In the 1212 structure Tl atoms are displaced towards the *a* and *b* axes, while in the 2201 and 2212 structures O and Tl atoms are displaced towards *ab* diagonals. Some papers (ref. [7], for instance) report that the direction of such a displacement is not always chosen unambiguously, when the *R*-factor is used as a criterion. Such a situation can be regarded as an inadequate structural model. Apparently,  $\text{Tl}^{3+}$  is not remarkably stereo specific when making up its oxygen environment. In this case the "trajectory" of Tl and/or O ion disorder can be more complicated than "splitting" into four closely located sites. A possible variant can be an equally probable (or almost equally probable) Tl and/or O ion distribution on circles with certain radii about a symmetrical site, as shown in figures 3c and 3d. These models are being refined now.

#### ABSTRACT

Four single crystals of Tl-containing superconducting 1212, 2201 and 2212 phases were studied by X-ray diffraction technique. We found that copper atoms partially occupy Tl sites. Besides, Ca is partially replaced by Tl in Ca-containing phases. Neither deficiency in oxygen site occupation nor extra-oxygen sites were detected. All the crystals exhibit Tl atom disordering and/or oxygen atom disordering in Tl-O layers. Atomic displacements from symmetrical sites in TlO layers can be interpreted as a possibility of making up a more appropriate environment for  $\text{Tl}^{3+}$  and  $\text{O}^{2-}$  ions. A correlation between structural features and superconducting properties is considered in terms of effective oxidation state of Cu.

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