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A New Member of the Thallium Superconductive Series, The "1212" Oxide $TlBa_2CaCu_2O_{8-y}$: Importance of Oxygen Content

M. HERVIEU, A. MAIGNAN, C. MARTIN, C. MICHEL, J. PROVOST, AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, Institut des Sciences de la Matière et du Rayonnement (ISMRa campus 2), Bd du Maréchal Juin, 14032 Caen Cedex, France

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A new superconductor was isolated and characterized by X-ray diffraction and electron microscopy. This oxide crystallizes in tetragonal system (*P*4/*mmm*) with the following parameters: a = 3.833 Å and c = 12.680 Å. A structural model was established from X-ray powder data. The structure is a new member of the family $(AO)_n(A'CuO_{3-y})_{n'}$ (A = Tl, Ba and A' = Ba, Ca) with n = 2 and n' = 2. It can be described as the intergrowth of double (AO) layers, rock salt-type, with double oxygen-deficient perovskite layers involving CuO_5 pyramids. The optimization of the thermal treatment and the importance of oxygen content are discussed. © 1988 Academic Press, Inc.

The recent investigations of the thallium copper oxides have shown that a large family of superconductors can be generated, which corresponds to the intergrowth of multiple distorted rock salt-type layers and multiple perovskite layers, according to the formulation $(AO)_n(A'CuO_{3-y})_{n'}$ (A = Tl, Ba; A' = Ba, Ca). Four members of this family have indeed been isolated: $Tl_2Ba_2CaCu_2O_{8+\delta}$ (n = 3, n' = 2) (*1–3*) called "2212" superconductivity below 107 K, $Tl_{2-x}Ba_2Ca_2Cu_3O_{10}$ (n = 3, n' = 3) (*4, 5*) called "2223" with a T_c of 125 K, $TlBa_2Ca_2Cu_3O_{10-y}$ (n = 2, n' = 3) (*6, 7*) called "1223" with a T_c of 120 K, and $TlBa_2CuO_{6-y}$ called "1201" superconductivity below 60 K (*8*). Our methods of synthesis using evacuated ampoules and barium peroxide have allowed these oxides to be isolated in the form of pure phases. We report here on a synthesis, structure, and superconducting properties of a new member of the series, $TlBa_2CaCu_2O_{8-y}$.

The oxide $TlBa_2CaCu_2O_{8-y}$ was prepared in the following way: a mixture of Tl_2O_3, BaO_2, CaO, and CuO was pressed in the form of pellets, placed in an alumina crucible, and heated in an evacuated silica ampoule at temperatures ranging from 780 to 820°C, and for various annealing times ranging from 5 to 6 hr. Under these conditions a pure phase could be isolated. The electron diffraction of this phase allowed its X-ray diffractogram to be indexed in a tetragonal cell with a = 3.833 Å and c = 12.68 Å, space group *P*4/*mmm*.

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TABLE I

$TlBa_2CaCu_2O_7$: CRYSTALLOGRAPHIC DATA

Atom	Site	x	y	z	B (Å^2)	τ
Tl	1(d)	0.5	0.5	0.5	1.0(4)	1.00(3)
Ba	2(g)	0.0	0.0	0.287(1)	0.1(4)	1.00(3)
CA[a]	1(a)	0.0	0.0	0.0	1.4(4)	1.00(5)
Cu	2(f)	0.5	0.5	0.130(2)	0.1(7)	0.95(7)
O1	4(i)	0.0	0.5	0.125(6)	1.0	1.00(7)
O2	2(h)	0.5	0.5	0.323(6)	1.0	1.00(7)
O3	1(b)	0.0	0.0	0.5	1.0	1.00(7)
O4	1(c)	0.5	0.5	0.0	1.0	0.00(7)

Note. Space group, *P4/mmm*; $R = 0.07$.
[a] 0.9 Ca + 0.1 Tl.

In order to establish a structural model for this phase, calculations of the intensities were performed on the 42 first peaks of the X-ray diffractogram, i.e., 32 *hkl*. Taking into account our previous results concerning these phases (*6*), the heavy atoms were initially placed in positions corresponding to the following sequence along **c**: "Tl–Ba–Cu–Ca–Cu–Ba–." After refinement of the positions of the metallic atoms, the oxygen atoms were placed in positions corresponding to double oxygen-deficient perovskite layers and single rock salt-type layers. The positions of the oxygen atoms and their occupancy factors were then successively refined. After final refinement of the atomic coordinates the discrepancy factor calculated on the intensities was lowered to $R = 0.07$ for the crystallographic data given in Table I. The positions of the oxygen atoms as well as their occupancy factors cannot be considered as accurate owing to the limited number of data obtained from an X-ray pattern. Nevertheless a structural model has been established without any ambiguity. The structure of $TlBa_2CaCu_2O_{8-y}$ (Fig. 1) can be described as formed of double-distorted rock salt-type layers intergrown with double-deficient perovskite layers. The rock salt-type layers are formed by a single TlO layer sandwiched by BaO layers according to the sequence "BaO–TlO–BaO." The oxygen-deficient perovskite layer is formed of single layers of CuO_5 corner-sharing pyramids interleaved by a plane of calcium ions. No oxygen seems to be present at the same level as the calcium ions in agreement with the short distance between the $[CuO_2]_\infty$ plane (3.3 Å) (Table II).

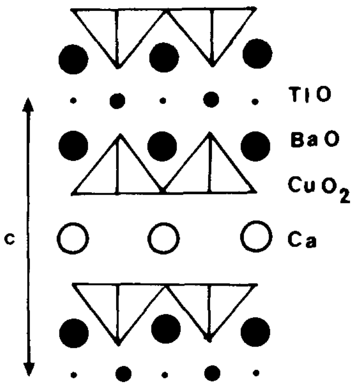

FIG. 1. Idealized drawing of the $TlBa_2CaCu_2O_7$ structure.

The formula of this oxide $TlBa_2CaCu_2O_7$ deduced from the structure implies a high Cu(III) content. The determination of critical temperature and of the fraction of diamagnetism performed with a vibrating sample magnetometer showed for this sample a critical temperature (midpoint) of 50 K (Fig. 2a) and a diamagnetic fraction of 20%. These results are to be compared to the oxide $Tl_2Ba_2CaCu_2O_{8+\delta}$ which exhibits, like $TlBa_2CaCu_2O_{8-y}$, a double "copper oxygen layer." This latter oxide exhibits a much

TABLE II

INTERATOMIC DISTANCES (Å)

Tl–O:	2.24 × 2 2.71 × 4	Ca–O:	2.49 × 8
Ba–O:	2.81 × 4 2.75 × 4 2.69 × 1	Cu–O:	1.92 × 4 2.45 × 1

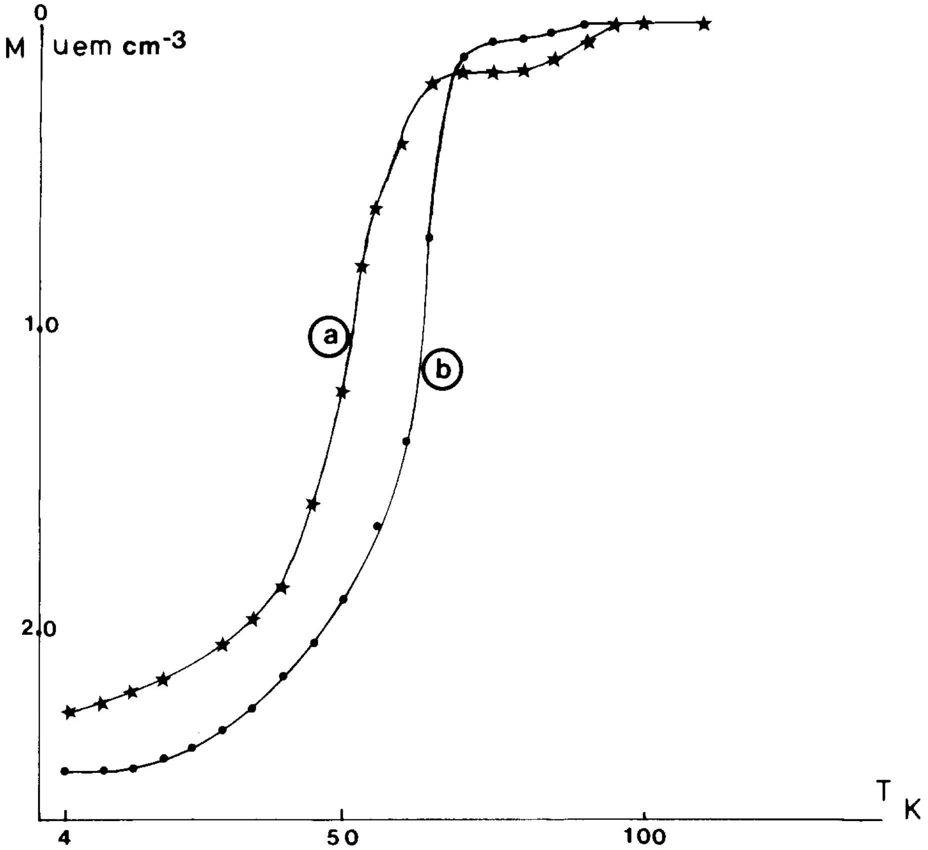

FIG. 2. Magnetization vs T for $TlBa_2CaCu_2O_7$ (a) after synthesis and (b) after annealing under inert gas flow.

higher critical temperature of 107 K and a much lower Cu(III) content, if one admits that thallium is in the trivalent state. This comparison suggests that a lowering of the oxygen content in $TlBa_2CaCu_2O_{8-y}$ should allow T_c to be increased. Annealing of the above sample in an inert atmosphere (argon flow) confirms this view: a midpoint temperature of 65 K (Fig. 2b) could be reached.

The role of the oxygen pressure used during the synthesis in the superconducting properties of these thallium compounds appears as a very important factor. In order to check its influence, the "2201" $Tl_2Ba_2CuO_{6+\delta}$ oxide was first prepared in an evacuated ampoule as described above using barium peroxide. A pure phase corresponding to the intergrowth of a single perovskite layer and a triple rock salt-type layer was isolated, but no superconductivity was observed. The annealing of this phase under an argon flow allowed a critical temperature of 30 K with a diamagnetic fraction of 11% to be reached, without any noticeable charge of the X-ray diffraction pattern.

These results clearly show that the thallium superconductors are so far not understood and that their superconducting properties could be improved by appropriate thermal treatments. They may differ from the lanthanide copper oxides by the fact that the thallium(III) layers could play the role of a reservoir of positive carriers which would induce a mixed valence Cu(II)–Cu(III) in the copper–oxygen layers. Systematical analysis of the oxygen content in all the thallium superconductors will be necessary to understand these phenomena.

References

1. R. M. M. Hazen, D. W. Finger, R. J. Angel, C. T. Prewitt, and C. G. Haidiacos, *Phys. Rev. Lett.*, to be published.
2. M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askev, R. B. Flippea, K. J. Morrissey, Y. Chondhry, and A. W. Sleight, *Nature (London)* **332** (1988).
3. A. Maignan, C. Michel, M. Hervieu, C. Martin, D. Groult, and B. Raveau, *Mod. Phys. Lett.*, in press (1988).
4. M. Hervieu, C. Michel, A. Maignan, C. Martin, and B. Raveau, *J. Solid State Chem.* **74**, 428 (1988).
5. S. Parkin, V. Y. Lee, E. M. Engler, A. I. Nazzal, J. C. Huang, G. Gorman, R. Savoy, and R. Beyers, *Phys. Rev. Lett.*, in press.
6. C. Martin, C. Michel, A. Maignan, M. Hervieu, and B. Raveau, *C.R. Acad. Sci.*, in press (1988).
7. S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers, and S. I. La Placa, submitted for publication.
8. M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdry, and A. W. Sleight, *Nature (London)*, in press.