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$Tl_{1-x}Pr_xSr_{2-y}Pr_yCuO_{5-\delta}$: First Member of the Family $TlA_2Ca_{m-1}Cu_mO_{2m+3}$ (A = Ba, Sr)

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Two series of superconductors have been synthesized since the discovery of superconductivity in the Tl–Ba–Ca–Cu–O system: the oxides $Tl_2Ba_2Ca_{m-1}Cu_mO_{2m+4}$ (*1–11*) and the oxides $TlA_2Ca_{m-1}Cu_mO_{2m+3}$ (A = Ba, Sr) (*12–21*). Both series belong to the same structural family, i.e., consist of an intergrowth of multiple oxygen-deficient perovskite layers (in which m corresponds to the number of copper slabs that form the perovskite layer) and of multiple rock-salt-type layers.

The two series differ from one another by the thickness of the rock salt layers: the first series, which can be denoted as Tl_2-cuprates characterized by triple rock-salt type layers, involve thallium bilayers, whereas the second series exhibit double rock-salt-type layers involving thallium monolayers. Until now, all the Tl_2-cuprates with m ranging from 1 to 4 have been isolated, whereas in the Tl_1-cuprates the first member $m = 1$ has not so far been reported. Such a phase, which would correspond to the composition $TlSr_2CuO_5$ or $TlBa_2CuO_5$, would have all copper in the Cu(III) state and thus would indeed be difficult to synthesize under normal oxygen pressure. We report here on the synthesis, structure, and superconducting properties of this first member obtained during the investigation of the Tl–Sr–Cu–O and Tl–Sr–Pr–Cu–O systems.

The two systems were prepared from mixtures of oxides Tl_2O_3, SrO_2, CuO, and/or Pr_6O_{11} in appropriate ratios. The intimate mixtures were then pressed into pellets, placed in alumina crucibles, and heated in evacuated silica ampoules at temperatures ranging from 750 to 860°C for 6 hr; the materials were then cooled in the furnace.

Under these experimental conditions two phases were isolated whose X-ray diffraction patterns were indexed in the tetragonal system, space group *P4/mmm*, in agreement with their electron diffraction patterns: $Tl_{0.8}Sr_{1.6}Pr_{0.6}CuO_5$ with a = 3,741 Å, c = 8,875 Å, and $Tl_{0.7}Sr_2Pr_{0.3}CuO_{5-\delta}$ with a = 3,733(5) Å, c = 8,951(7) Å.

In the system Tl–Sr–Cu–O, the isostructural phase could not be isolated. Nevertheless, it was observed in a mixture with an unknown phase of nominal composition Tl Sr_2CuO_x, suggesting a composition $TlSr_2$ $CuO_{5-\delta}$ (a = 3.743 Å, c = 8.921 Å).

In order to check out the structural model corresponding to the first member of the series $TlSr_2Ca_{m-1}Cu_mO_{2m+3}$, structure calculations were performed from X-ray powder data of the oxide $Tl_{0.8}Sr_{1.6}Pr_{0.6}$

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TABLE I

$Tl_{0.8}Pr_{0.6}Sr_{1.6}CuO_{5-\delta}$: CRYSTAL DATA SPACE GROUP $P4/mmm$

		x	y	z	B
$Tl_{0.8}Pr_{0.2}$	(1b)	0	0	$\frac{1}{2}$	0.9
$Sr_{1.6}Pr_{0.4}$	(2h)	$\frac{1}{2}$	$\frac{1}{2}$	0.205(1)	0.3
Cu	(1a)	0	0	0	0.3
O(1)	(2g)	0	0	0.259(5)	0.1
O(2)	(1d)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.1
O(3)	(2f)	$\frac{1}{2}$	0	0	0.1

TABLE II

$Tl_{0.8}Pr_{0.6}Sr_{1.6}CuO_{5-\delta}$: INTERATOMIC DISTANCES (Å)

Tl(Pr)–O:	2.14 ×2	Cu–O:	1.87 ×4
	2.64 ×4		2.29 ×2
Sr(Pr)–O:	2.69 ×4		
	2.61 ×4		
	2.61 ×1		

CuO_5, using the first (32) reflections, i.e., (43) *hkl*. After refinement of the atomic coordinates, of thermal factors, and finally of the occupancy factors, the discrepancy factor based on the intensities was lowered to $R = 0.07$ for the data given in Table I. From these results it is clear that this phase does represent the first member of the series: its structure (Fig. 1a) corresponds to an intergrowth of a single perovskite layer $[(Sr, Pr)_1 CuO_3]_\infty$ with a doubler rock-salt-type layer $[(Tl, Pr, Sr)_2O_2]_\infty$. It is worth pointing out that La_2CuO_4-type oxides (Fig. 1b) and $Tl_2 Ba_2CuO_6$ (Fig. 1c) exhibit similar single perovskite layers and differ from this new phase by the thickness of their rock-salt-type layers which are single for the former and triple for the latter.

The refinement of the occupancy factors shows that the thallium monolayers are partly occupied by praseodymium, in agreement with the interatomic distances (Table II), suggesting the presence of Pr(IV) on those sites whose size is similar to that of Tl(III). On the other hand, the praseodymium ions located in the strontium layers may be in either the Pr(IV) or the Pr(III) configuration. This leads to the formulation $(Tl_{0.8}Pr_{0.2})(Sr_{1.6}Pr_{0.4})CuO_{5-\delta}$ $(0 \leq \delta < 0.2)$.

Magnetic measurements performed with a vibrating sample magnetometer and a SQUID magnetometer show only traces of diamagnetism for $Tl_{0.7}Pr_{0.3}Sr_2CuO_{5-\delta}$ and $TlSr_2CuO_{5-\delta}$; by contrast it is observed (Fig. 2) that $Tl_{0.8}Pr_{0.6}Sr_{1.6}CuO_{5-\delta}$ exhibits diamagnetism below 40 K and 2% of the Meisner effect at 4 K. These results show clearly that this oxide is a potential superconductor, even though praseodymium is not generally favorable to superconductivity owing to the formation of Pr(IV). The T_c

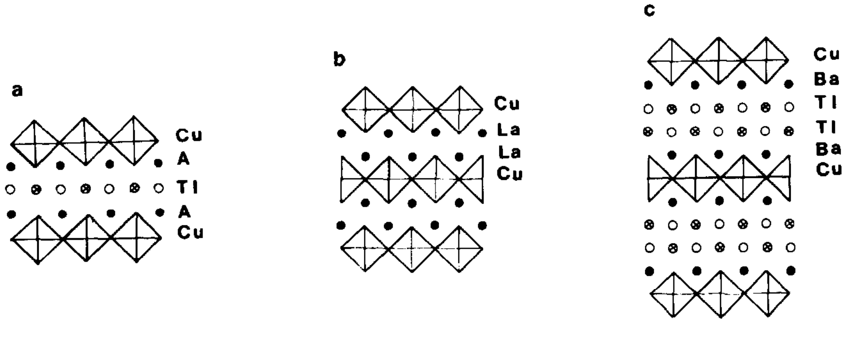

FIG. 1. Schematized structure of $Tl_{0.8}Pr_{0.6}Sr_{1.6}CuO_{5-\delta}$ (a) compared to those of La_2CuO_4-type oxides (b) and of $Tl_2Ba_2CuO_6$ (c).

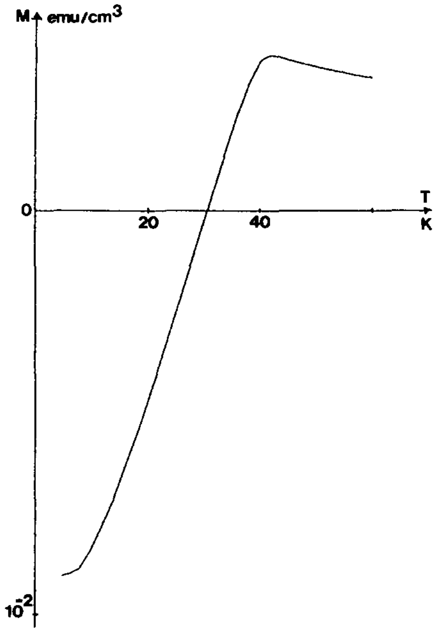

FIG. 2. Magnetic susceptibility versus temperature for $Tl_{0.8}Pr_{0.6}Sr_{1.6}CuO_{5-\delta}$ at B-50 Gauss.

value near 40 K is close to those observed for superconductors characterized by single perovskite layers, i.e., La_2CuO_4-type oxides ($T_c \approx 40$ K) and $Tl_2Ba_2CuO_6$ ($T_c \approx 65$ K). The control of the experimental conditions of synthesis and the investigation of similar formulations involving other rare-earth elements should lead to an improvement in the superconducting properties of this new member.

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