

Structure of the New $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ by Rietveld Analysis†

Tsong- Jen Lee¹, Hoong-Kun Fun¹, Arlohun Wang¹, Cheng-Hung Chou¹,
Chiou-Chu Lai², and H. C. Ku¹

¹ *Department of Physics, National Tsing Hua University,
Hsinchu, Taiwan 300, R. O. C.*

² *Institute of Electronics, National Chiao-Tung University,
Hsinchu, Taiwan 300, R. O. C.*

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The crystalline structure of new $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-y}$ was obtained at room temperature from X-ray powder diffraction with $\text{CuK}\alpha$ radiation using Rietveld analysis. $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ is semiconducting at room temperature with a $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ type (1212) structure (space group P4/mmm) and cell parameters $a = 3.91836(3) \text{ \AA}$, $c = 12.5498(2) \text{ \AA}$. The structure was refined for 15 parameters to $R_{wp} = 6.89 \%$, $R_p = 5.09 \%$ for 6323 step intensities and $R_b = 13.24 \%$ for 138 reflections.

I. INTRODUCTION

New $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-x}$ (1212) type of compounds with the formula $\text{TlBa}_2\text{RCu}_2\text{O}_{7-x}$ were successfully synthesized, with $\text{R} = \text{Y, Nd, Gd, Pr, Sm, Dy, Er}$ [1-5]. The antiferromagnetic Neel temperature $T_n = 8 \text{ K}$ and magnetic order as well as superconductivities have been studied [5-6] for Pr-substituted compounds $\text{TlBa}_2(\text{Pr}_{1-y}\text{Ca}_y)\text{Cu}_2\text{O}_{7-y}$. Electrical resistivity measurements showed that $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ is semiconducting at room temperature with $\rho = 9.6 \text{ K}\Omega\cdot\text{cm}$ (room temperature) and $\rho = 21.3 \text{ K}\Omega\cdot\text{cm}$ ($T = 256 \text{ K}$), showing no superconductivity [5]. The measurements showed no superconductivity of $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ till $T = 2 \text{ K}$ for $x \geq 0.5$ [6].

This article presents the structural parameters of $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ by Rietveld analysis, which reveals the resembling structure to $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-x}$ (1212) type such as $\text{TlBa}_2\text{YCu}_2\text{O}_{7-x}$ [6].

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II. EXPERIMENTAL

$\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ compound was prepared by baking at 870 °C for 10 h with the starting ratio $\text{Tl}:\text{Ba}:\text{Pr}:\text{Cu}=1.2:2:1:2$. High purity of Tl_2O_3 , BaO_2 , Pr_6O_{11} and CuO were used for this synthesis [5].

(510)-cut Si wafer was chosen as the substrate of powder sample holder. It ensures there is no any other crystalline or amorphous peak during data collecting. $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ powder was pasted to the sample holder with petroleum jelly to minimize the possible preferred orientation in the sample. The distribution of the powder should be very homogeneous over the effective area of X-ray illumination, otherwise the collected data would not be good enough for refinement.

The diffraction data for Rietveld analysis were collected at room temperature by the Rigaku Rotaflex RTP 500 RC powder diffractometer with a Bragg-Brentano geometry, diffracted-beam graphite (0002) monochromator, $\text{CuK}\alpha$ radiation, step-scan-size of 0.02° , counting time 10 sec., divergence slit $\text{DS}=1.7$ mm, anit-scattering slit $\text{AS}=1.7$ mm, receiving slit $\text{RS}=0.6$ mm. The data were collected over the range from $10^\circ - 140^\circ$. 150 reflections were reported.

Rietveld analysis program version DBWS-9006PC (release 12.8.91) [7-8] was used. The background was refined with a fifth order of polynomial. The profile was refined with pseudo-Voigt function. The preferred orientation (001) was refined with Rietveld-Toraya function. No absorption correction was taken into account. The thermal parameters could be refined to the reasonable values if they are tied together. Quoted values from the reference [1] were used as the initial parameters. 6323 data and 138 reflections were used. 15 parameters were refined. The wave lengths of the $\text{CuK}\alpha_1$, $\text{CuK}\alpha_2$ and the intensity ratio were chosen as 1.5406 Å, 1.5444 Å and 0.514.

The refined structure parameters are listed in Table I, II. and III. The data, fitting curve and the differences (residual: $I_{obs} - I_{cal}$) are shown in Fig. 1. The numbers in the parentheses in Table I are the estimated standard deviations, whereas they are omitted in Table II and III. x, y, z are the fractional coordinates. B_{iso} is the isotropic thermal parameter. R-values are defined as follows:

$$R_{wp} = \left[\frac{\sum w_i (Y_{io} - Y_{ic})^2}{\sum w_i Y_{io}^2} \right]^{1/2}, \quad R_p = \frac{\sum |Y_{io} - Y_{ic}|}{\sum Y_{io}}, \quad R_b = \frac{\sum |I_{ko} - I_{kc}|}{\sum I_{ko}},$$

where Y_{io} and Y_{ic} are observed and calculated intensities at step i , I_{ko} and I_{kc} are the peak intensities observed and calculated for reflection k , w_i is the weight ($= 1/Y_{io}$).

TABLE I. Structure parameters and R values of $\text{TlBa}_2\text{Cu}_2\text{O}_{7-x}$

Space group	P4/mmm			$Z = 1$		
Cell parameters	a = 3.91836(6) c = 12.5498(2)			\AA A		
Atom	Position	x	y	z	Occupancy	$B_{iso}(\text{\AA}^2)$
Tl	1a	0	0	0	0.940(3)	1.64(1)
Ba	2h	1/2	1/2	0.2078(1)	1	0.11(1)
Pr	1d	1/2	1/2	1/2	1	0.13(1)
cu	2g	0	0	0.3622(2)	1	0.13(1)
O(1)	4i	0	1/2	0.3791(6)	1	0.27(1)
O(2)	2g	0	0	0.1666(7)	1	0.33(1)
O(3)	1c	1/2	1/2	0	0.93(2)	0.65(1)
R-values	$R_{wp} = 6.89 \%$,			$R_p = 5.09 \%$	and	$R_b = 13.24 \%$

TABLE II. Atom positions of $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ with one formula in unit cell:space group: P4/mmm

Complex	Atom	Site	Vertical Position (A)	x	y	z
TlO	Tl	1a	12.5498	0	0	1
	O(3)	1c	12.5498	1/2	1/2	1
OBa	O(2)	2g	10.4590	0	0	0.8334
	Ba	2h	9.9420	1/2	1/2	0.7922
CuO ₂	Cu	2g	8.0043	0	0	0.6378
	O(1)	4i	7.7922	0	1/2	0.6209
	O(1)	4i	7.7922	1/2	0	0.6209
Pr	Pr	1d	6.2749	1/2	1/2	1/2
	O(1)	4i	4.7576	1/2	0	0.3791
	O(1)	4i	4.7576	0	1/2	0.3791
CuO ₂	cu	2g	4.5455	0	0	0.3622
	Ba	2h	2.6078	1/2	1/2	0.2078
OBa	O(2)	2g	2.0908	0	0	0.1666
	O(3)	1c	0.0000	1/2	1/2	0
TlO	Tl	1a	0.0000	0	0	0

TABLE III. Selected interatomic distances (Å)

Pr-O(1)	2.478	Cu-O(1)	1.971
Ba-O(1)	2.909	cu-O(2)	2.455
Ba-O(2)	2.819	Tl-O(2)	2.091
Ba-O(3)	2.608	Tl-O(3)	2.771

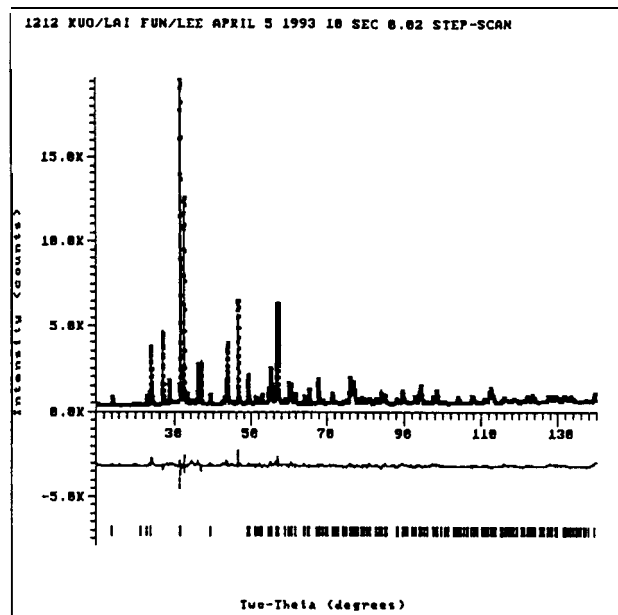


FIG. 1. Observed (dotted), calculated (solid-line) data and residual of the powder diffraction pattern of $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$. Residual is the difference between observed and calculated data: $I_{obs} - I_{cal}$. The marks in the bottom of the figure indicate the reflections used for the refinement.

III. RESULTS AND DISCUSSIONS

The structure was refined with space group $P4/mmm$. The refined parameters and atom positions are listed in Table I, II and III. There are 7 atoms in a unit cell. Each occupies the similar position with that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123) tetragonal structure [9] except the oxygen atom O(3) in TlO-plane. Tl replaces Cu at (0,0,0). Oxygen O(3) occupies the basal

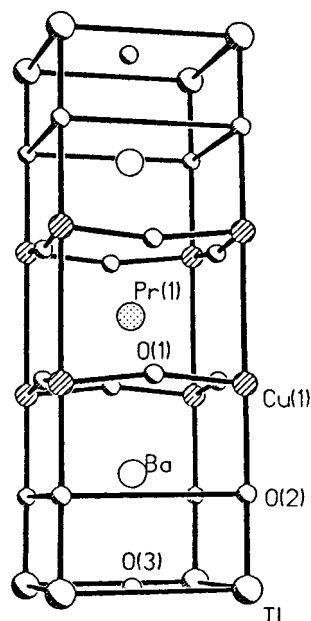


FIG. 2. The structure of $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ (1212). Only oxygen O(3) is different from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123) tetragonal structure occupying the basal plane centre $(1/2, 1/2, 0)$ rather than the edge centre $(0, 1/2, 0)$.

plane centre $(1/2, 1/2, 0)$ rather than the edge centre $(0, 1/2, 0)$. Fig. 2 shows the schematic positions.

The isotropic thermal parameters of atom Tl and O(3) are larger than the others. It is quite coincided with fact that Tl is volatile in the compound and there is some deficiency of oxygen in site $(1/2, 1/2, 0)$. The occupancy number is 0.94 for Tl atom and that is about 0.93 for O(3) atom. So the x is about 0.07 in the formula $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$. The other sites of the atom position refined to 1, i.e., fully occupied.

By examining the atomic coordinates in Table II, all the atoms in $\text{TlBa}_2\text{PrCu}_2\text{O}_{7-x}$ are further from Pr atom than those in $\text{TlBa}_2\text{YCu}_2\text{O}_{7-x}$ from Y atom. In fact, as shown in Table III, Pr-O(1) bond length in this article is 2.478 Å, larger than Y-O(1) bond length 2.4045 Å in $\text{TlBa}_2\text{YCu}_2\text{O}_{7-x}$ [1]. This results in the cell parameters a , c being larger than those in reference [1].

One may find that the positions of the oxygen atoms have less precision than other atoms. That is because oxygen atom is very light and not sensible to X-ray diffraction data. The precision and accuracy about Rietveld analysis were discussed recently [10]. Further Rietveld analysis studies on $\text{Tl}(\text{Ba}_{2-y}\text{Sr}_y)\text{PrCu}_2\text{O}_{7-x}$ compounds are underway.

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