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Low-temperature unit-cell parameters of $La_{1-x}Pr_xCaBaCu_3O_7$ compounds

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The suppression of the superconductivity by praseodymium in $La_{1-x}Pr_xCaBaCu_3O_7$ may be explained in terms of the difference in the electronic or crystal structure between these compounds. Three compositions with $x = 0.0$, 0.5, 1.0 were, therefore, investigated by X-ray diffraction in order to determine the unit-cell dimensions at room temperature as well as at lower temperatures down to 5 K. The results showed no considerable changes in the orthorhombic unit-cell dimensions on decreasing the temperature to 5 K. Unit-cell volumes at low temperatures were 0.99 of the room temperature values. The intensity sequence of reflections in the diffraction pattern was the same for all samples throughout the range of temperature studied.

1. Introduction

As in the case of $Y_{1-x}Pr_xCu_3O_{7-\delta}$, an increase of praseodymium suppresses the superconductivity of $La_{1-x}Pr_xCaBaCu_3O_7$ and leads to a decrease in T_c near 0 K at $x \simeq 0.6$. In addition, there is a change in normal-state resistivity, $\rho(T)$, from metallic to semiconducting behaviour at $x = 0.4$ [1]. Similar behaviour was observed for $La_{1-x}Pr_xBaCu_3O_{7-\delta}$ [2] and $La_{1-x}Pr_xBaCaO_{7-\delta}$ [3]. For the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ there is a considerable increase in the lattice parameters with increasing x [1, 6]. The average lattice parameters in the *ab* plane increase from 0.386 nm when $x = 0.0$ to 0.389 nm when $x = 1.0$. Such behaviour was not observed for $La_{1-x}Pr_xCaBaCu_3O_7$. The average lattice parameters in the *ab* plane are almost constant over the range $0 < x < 1$, while c shows a minimum value at $x \simeq 0.5$. Suppression of the superconductivity by praseodymium in such compounds, although they have an orthorhombic structure isomorphic to that of $YBa_2Cu_3O_{7-\delta}$, can be explained in terms of the difference in the electronic or crystal structures between the compounds.

The purpose of the present work was to investigate the variation of lattice constants at room temperature, as well as at lower temperature down to 5 K for the compound $La_{1-x}Pr_xCaBaCu_3O_7$ for three values of x, i.e. $x = 0.0$, 0.5, and 1.0.

2. Experimental procedure

2.1. Sample preparation

The same polycrystalline samples of $La_{1-x}Pr_xCaBaCu_3O_7$ compounds which were used in previous work [7] were used in the present low-temperature X-ray investigations.

2.2. X-ray measurements

The X-ray experiments were performed using a Philips PW 1050 vertical diffractometer in conjunction with a copper target ($\lambda = 0.1542$ nm) and a graphite curved-

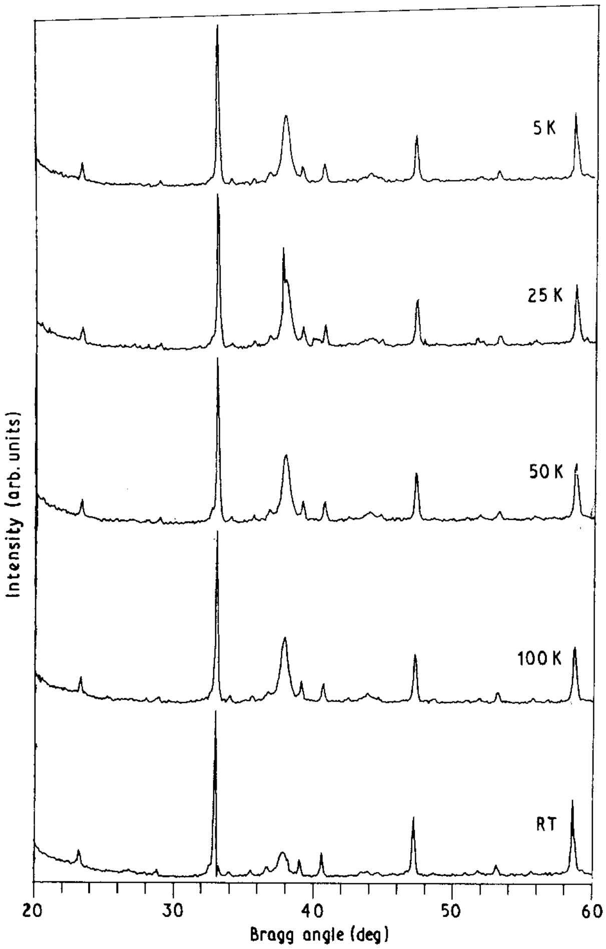

Figure 1 X-ray diffraction patterns for $La_{1-x}Pr_xCaBaCu_3O_7$ compound with $x = 0.0$ at different temperatures.

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crystal monochromator. Measurements were taken from room temperature down to 5 K, using a flow-type cryostat (CF108) where there was no direct contact between the sample and the liquid gas, i.e. only the sample and its holder were in the beam which passes through the sample window. The range of scattering $5° < 2\theta < 90°$ was covered in 0.1° steps ($\Delta 2\theta$).

3. Results, analysis and discussion

Figs 1–3 show the X-ray diffraction patterns for the $La_{1-x}Pr_xCaBaCu_3O_7$ crystalline compounds with $x = 0.0$, 0.5 and 1.0 at different temperatures.

As reported previously [7], the compounds are metallic at higher temperatures. Those with $x \leqslant 0.5$ become superconducting below a certain critical transition temperature (T_c) as shown in Fig. 4, and those with $x > 0.5$ become semiconducting at lower temperatures. The compounds have an orthorhombic unit cell of space group $Pmmm$-(D^1_{2h}) at room temperature.

The present X-ray diffraction patterns indicate that the compounds have an orthorhombic unit cell at lower temperatures, down to 5 K.

Figs 1–3, indicate that the diffraction pattern in the region $36° < 2\theta > 42°$ at room temperature for the compound with $x = 0.5$ is different from that of the compounds with $x = 0.0$ and 1.0. As reported earlier [7], this compound represents the end of the superconductivity in the $La_{1-x}Pr_xCaBaCu_3O_7$ compounds.

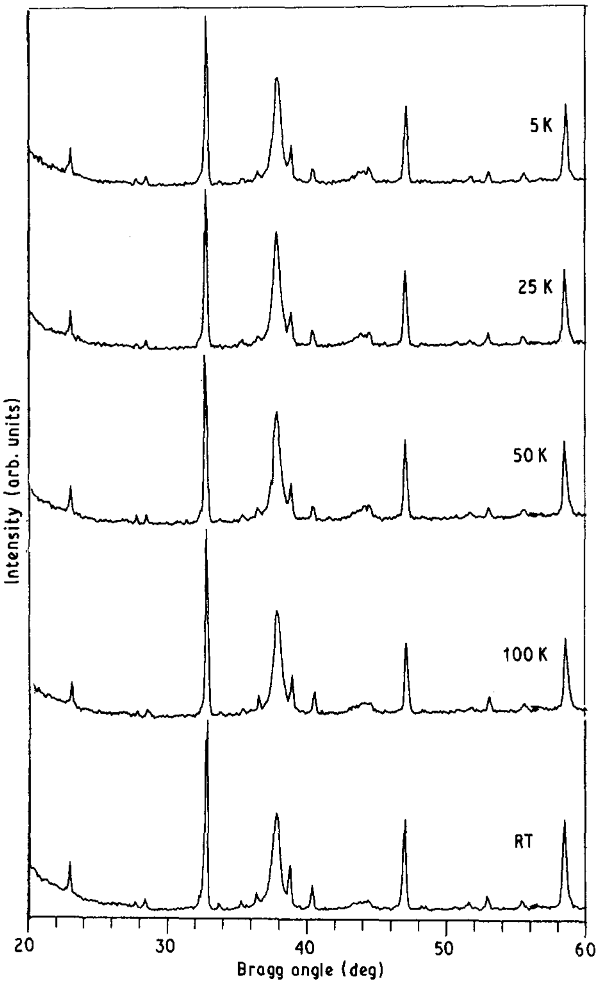

Figure 2 X-ray diffraction patterns for $La_{1-x}Pr_xCaBaCu_3O_7$ compound with $x = 0.5$ at different temperatures.

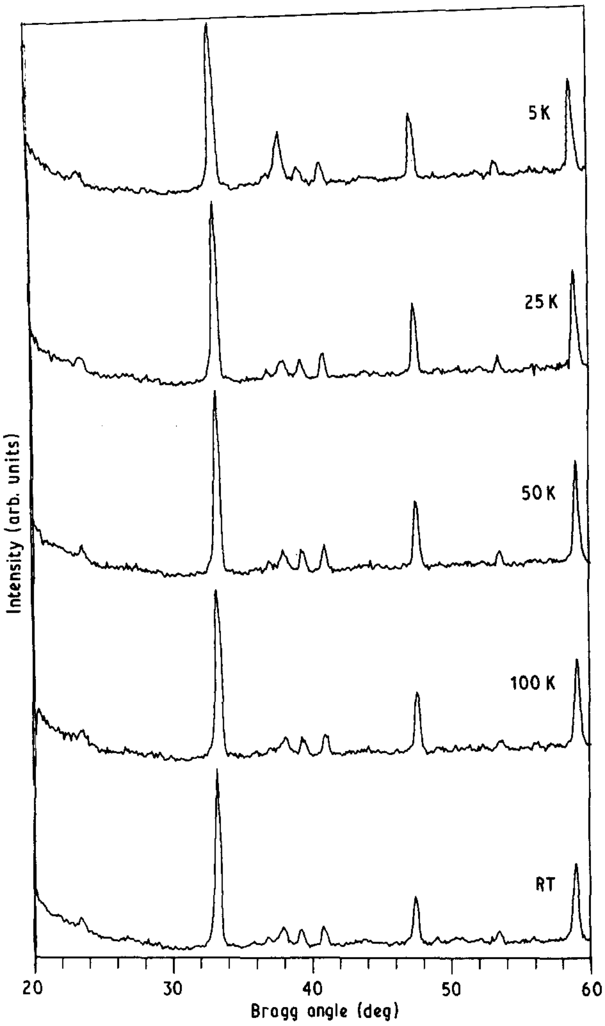

Figure 3 X-ray diffraction patterns for $La_{1-x}Pr_xCaBaCu_3O_7$ compound with $x = 1.0$ at different temperatures.

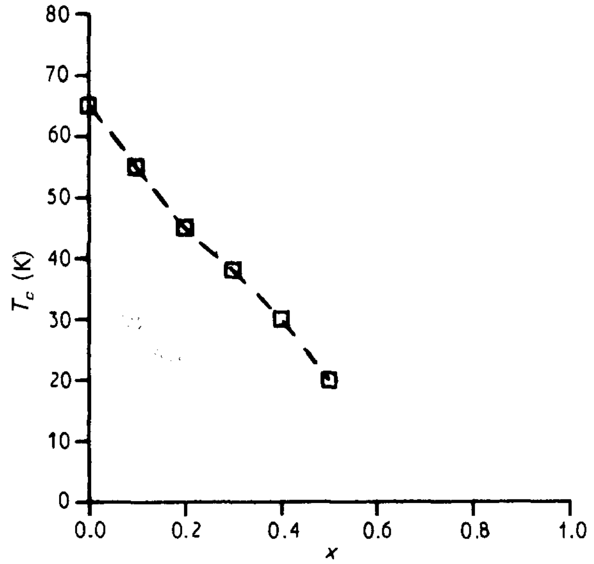

Figure 4 The critical transition temperature, T_c, of $La_{1-x}Pr_x$-$CaBaCu_3O_7$ compound as a function of x.

Tables I–III indicate the present measurements of Bragg angles, d-spacings, lattice parameters and unit-

TABLE I Bragg angles (2θ), *d*-spacings and lattice parameters for $La_{1-x}Pr_xCaBaCu_3O_7$ compound with $x = 0.0$

Lattice parameters	*hkl* l.p.	RT		100 K		50 K		25 K		5 K	
		2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)
	0 0 3/0 1 0	23.4	0.3819	23.5	0.3807	23.5	0.3807	23.5	0.3807	23.5	0.3807
	1 0 3/1 1 0	33.1	0.2701	33.2	0.2726	33.2	0.2726	33.2	0.2726	33.2	0.2726
	0 2 0/0 0 6	47.4	0.1950	47.5	0.1904	47.5	0.1904	47.5	0.1904	47.5	0.1904
	1 1 6/1 2 3	58.9	0.1565	59.0	0.1561	59.0	0.1561	59.0	0.1561	59.0	0.1561
a		0.3819 nm		0.3905 nm							
b		0.3899 nm		0.3807 nm							
c		1.1458 nm		1.1422 nm							
V		0.1706 nm^3		0.1698 nm^3							
				$V_{LT}/V_{RT} = 0.99$							

TABLE II Bragg angles (2θ), *d*-spacings and lattice parameters for $La_{1-x}Pr_xCaBaCu_3O_7$ compound with $x = 0.5$

Lattice parameters	*hkl* l.p.	RT		100 K		50 K		25 K		5 K	
		2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)	2θ (deg)	*d*(nm)
	0 0 3/0 1 0	23.0	0.3868	23.1	0.3855	23.1	0.3855	23.1	0.3855	23.1	0.3855
	1 0 3/1 1 0	33.8	0.2739	33.8	0.2739	33.8	0.2739	33.8	0.2739	33.8	0.2739
	0 2 0/0 0 6	47.0	0.1934	47.1	0.1928	47.1	0.1928	47.1	0.1928	47.1	0.1928
	1 1 6/1 2 3	58.4	0.1580	58.5	0.1576	58.5	0.1576	58.5	0.1576	58.5	0.1576
a		0.3878 nm		0.3893 nm							
b		0.3867 nm		0.3855 nm							
c		1.1602 nm		1.1565 nm							
V		0.1740 nm^3		0.1735 nm^3							
				$V_{LT}/V_{RT} = 0.99$							

TABLE III Bragg angles (2θ), *d*-spacings and lattice parameters for $La_{1-x}Pr_xCaBaCu_3O_7$ compound with $x = 1.0$

Lattice parameters	*hkl* l.p.	RT		100 K		50 K		25 K		5 K	
		2θ (deg)	*d* (nm)	2θ (deg)	*d* (nm)	2θ (deg)	*d* (nm)	2θ (deg)	*d* (nm)	2θ (deg)	*d* (nm)
	0 0 3/0 1 0	23.2	0.3843	23.4	0.3831	23.3	0.3831	23.3	0.3831	23.3	0.3831
	1 0 3/1 1 0	33.0	0.2733	33.0	0.2735	33.0	0.2735	33.0	0.2735	33.1	0.2735
	0 2 0/0 0 6	47.2	0.1922	47.2	0.1915	47.2	0.1915	47.3	0.1915	47.3	0.1915
	1 1 6/1 2 3	58.6	0.1572	58.7	0.1569	58.7	0.1569	58.7	0.1569	58.7	0.1569
a		0.3889 nm		0.3906 nm							
b		0.3843 nm		0.3831 nm							
c		1.1529 nm		1.1493 nm							
V		0.1723 nm^3		0.1720 nm^3							
				$V_{LT}/V_{RT} = 0.99$							

cell volumes for the $La_{1-x}Pr_xCaBaCu_3O_7$ crystalline compounds at different temperatures.

The average difference between the lattice parameter values measured in the present work at room temperature and those measured previously [7] for the same compounds is nearly 0.8%. This may be due to the difference in experimental arrangements. The present measurements were performed while the samples were inside the cryostat and using a step-scanning technique, while in the previous work the samples were attached to an aluminium holder and a continuous scanning technique was used.

At low temperatures, i.e. at 100, 50, 25 and 5 K, the measured Bragg angles of a given reflection for each sample were almost the same. Tables I–III indicate constant lattice parameters throughout the measured low-temperature range. The calculated unit-cell volume of each compound at low temperatures is ≈0.99% of that at room temperature.

Tables IV–VI show the measured intensities of some reflections at different temperatures. The tables indicate that the strongest line is 1 0 0/1 0 3 for all *x* values at room temperature as well as at low temperatures, exactly as in the previous work [7]. The intensity sequence is the same for all samples at all temperatures, indicating the absence of any definite phase transition at low temperatures.

TABLE IV Relative intensity (arb. units) for $La_{1-x}Pr_xCaBaCu_3O_7$ with $x = 0.0$

hkl	RT	100 K	50 K	25 K	5 K
0 0 3/0 1 0	3.47	3.61	3.58	7.34	4.40
1 0 3/1 1 0	100.00	100.00	100.00	100.00	100.00
0 2 0/0 0 6	14.66	23.61	27.90	27.33	29.37
1 1 6/1 2 3	35.40	40.51	48.50	51.59	45.58

TABLE V Relative intensity (arb. units) for $La_{1-x}Pr_xCaBaCu_3O_7$ with $x = 0.5$

hkl	RT	100 K	50 K	25 K	5 K
003/010	7.03	7.35	9.95	8.77	9.55
103/110	100.00	100.00	100.00	100.00	100.00
020/006	36.23	37.07	34.81	33.25	42.67
116/123	48.13	42.22	45.25	34.13	48.99

TABLE VI Relative intensity (arb. units) for $La_{1-x}Pr_xCaBaCu_3O_7$ with $x = 1.0$

hkl	RT	100 K	50 K	25 K	5 K
003/010	5.47	4.41	5.52	3.82	4.62
103/110	100.00	100.00	100.00	100.00	100.00
020/006	26.02	22.05	21.06	25.14	18.59
116/123	46.64	36.25	40.00	33.17	29.68

4. Conclusion

It is clear that $LaCaBaCu_3O_{7-\delta}$ and $La_{1-x}Pr_xCaBaCu_3O_7$ are derived from $YBa_2Cu_3O_{7-\delta}$ by possible substitution of Y^{3+} by Ca^{2+} and Ba^{2+} [3]. This leads to randomization of the position of lanthanum and calcium ions. Such randomization becomes more probable when the sizes are similar, as in the case of the calcium and praseodymium ions, and may explain the relative constancy of the lattice parameters over the entire range of x studied and at different temperatures down to 5 K. This lattice parameter constancy is not present in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

The decrease in T_c of such a system with increasing x [3] and the constancy of the lattice parameters, i.e. the quenching of superconductivity, can be explained by the mixed-state values of the praseodymium ion in the investigated structure, as in the case of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ [1].

The presence of praseodymium ions would decrease the number of holes in the CuO_2 planes. This will be reflected by the transition into the normal state from metallic to semiconducting as x increases, and the complete quenching of the superconductivity as x exceeds 0.5–0.6.

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