

## STRUCTURAL REFINEMENT OF $[Y_{0.75}Ca_{0.25}]SrBaCu_{3-x}(PO_4)_xO_y$

J.C. González González, D.A. Landinez Tellez, J. Albino Aguiar y A. Bustamante Domínguez

Laboratorio de Superconductividad, Facultad de Ciencias Físicas, Universidad Nacional Mayor de San Marcos,  
Apartado Postal 14-0149, Lima 14 - PERU

Laboratorio de Superconductividad, Departamento de Física, Universidad Federal de Pernambuco, 50670-901 Recife  
PE, BRASIL.

**ABSTRACT:**  $(PO_4)^{3-}$  doped  $[Y_{0.75}Ca_{0.25}]SrBaCu_{3-x}(PO_4)_xO_y$  compounds with  $0.00 \leq x \leq 0.30$  were synthesized using the solid state reaction technique at normal pressure and temperature conditions. The X-ray diffraction patterns show that for  $x = 0.0$  the samples crystallize into an orthorhombic phase, and for other  $x$  values the samples presented a tetragonal structure. The Rietveld method was used to refine the lattice constants. The analysis of structure with Rietveld refinement was done using a model that contains one  $Cu(2)$  in a four coordination and not in five coordination in the other 123 tetragonal structures. All samples are superconductors as reported previously [1].

**Keywords:** synthesis, Rietveld refinement, superconductivity, phosphate.

**SUMILLA:** Se sintetizaron compuesto de  $[Y_{0.75}Ca_{0.25}]SrBaCu_{3-x}(PO_4)_xO_y$  dopados con  $(PO_4)^{3-}$ , para  $0.0 \leq x \leq 0.30$  usando la técnica de reacción de estado sólido en condiciones de presión y temperatura normales. El patrón de difracción de rayos-X muestra que para  $x = 0,0$  las muestras cristalizan en una fase ortorrómbica y para otros valores de  $x$  las muestras presentan una estructura tetragonal. Se utilizó el método de Rietveld para refinar las constantes reticulares. El análisis de estructura con refinamiento de Rietveld se hizo usando un modelo que contiene un  $Cu(2)$  en coordinación -4 y no en coordinación -5 como en las otras estructuras tetragonales 123. Todas las muestras son superconductoras como se ha reportado anteriormente [1].

**Palabras Claves:** síntesis, refinamiento de Rietveld, superconductividad, fosfato.

### 1. INTRODUCTION

It has been found that  $(PO_4)^{3-}$  substitution into the Y-123 structure can be achieved successfully to form superconducting phases with the typical composition  $[Y,Ca]SrBaCu_{3-x}(PO_4)_xO_y$  [2-5]. The superconducting framework would be expected to be less amenable to substitution of the tetrahedral ion, and this may account for the slightly different structural chemistry of the material. High microscope resolution [6] has revealed that the  $(PO_4)^{3-}$  group has still a tendency to order into discrete chains, but in these phases only about 25 % of the  $CuO$  chains can be substituted, while the remaining chain  $Cu$  atoms retain their square planar coordination.

The incorporation of oxyanions into copper oxide frameworks has provided a wealth of new possibilities for the synthesis of new materials with modified electronic and structural features.

Here we report the results on the effect of the incorporation of a phosphate group into the Y-123 structure and simultaneous replacement of  $Y^{3+}$  by  $Ca^{2+}$  ions, prepared under ambient conditions.

### 2. EXPERIMENTAL PROCEDURES

The samples were prepared using the standard solid state reaction technique. The detailed procedures for sample preparation were described elsewhere [7]. Briefly, pure  $Y_2O_3$ ,  $CuO$ ,  $BaO$ ,  $SrCO_3$ ,  $CaCO_3$  and  $NH_4H_2PO_4$  were weighed and mixed according to the chemical formula of  $[Y,Ca]SrBaCu_{3-x}(PO_4)_xO_y$  (YCSBCPO), with  $x = 0.00, 0.10, 0.15, 0.20, 0.25, 0.30$ . Each of these mixtures was ground for several tens of minutes. Afterwards, they were put into a furnace and annealed at 1000 C in oxygen flow for about 16 hours. The resultant powders were reground and pelletized into disk-shaped pellets, and annealed again for another 16 hours twice. Finally the products were cooled to room temperature.

$T_c$  was determined using the first derivative of the susceptibility curve. The  $T_c$  transition width ( $\Delta T_c$ ) was defined as the width of the curve for the first derivative. The powder X-ray diffraction (XRD) patterns of  $[Y_{0.75}Ca_{0.25}]SrBaCu_{3-x}(PO_4)_xO_y$  are shown in figure

1. The sample with  $x = 0.0$  presents the main characteristic peaks of the orthorhombic phase (Pmmm).

Additionally, one obtains a typical tetragonal phase (P4/mmm) diffractogram for the other ones. These results are similar to those obtained by Marimuthu *et al* [8].

The standard analyzing program named DBWS9807 was used to perform Rietveld refinements. The background was refined using a fifth-degree polynomial. A pseudo-Voigt function by linear combination of Gaussian and Lorentz shapes was used to describe the reflection profiles.

No absorption and micro-absorption corrections were applied to the raw data. The wavelengths of  $\text{CuK}_{\alpha 1}$ ,  $\text{CuK}_{\alpha 2}$  and the intensity ratio were 1,54050 Å; 1,54430 Å and 0,500, respectively.

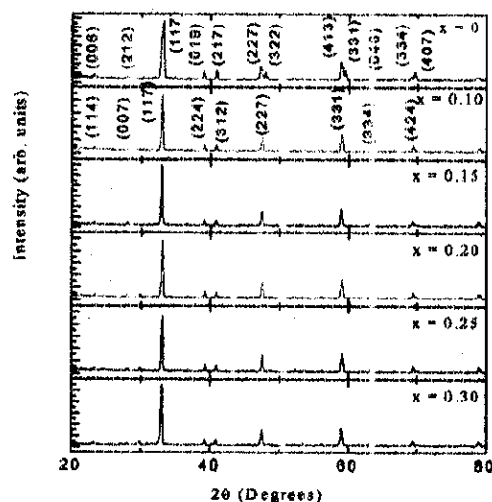


Figure 1. Powder X-ray diffraction patterns of  $[\text{Y}_{0.75}\text{Ca}_{0.25}]\text{SrBaCu}_{3-x}(\text{PO}_4)_x\text{O}_y$

The “R-factors”,  $R_p$  and  $R_{wp}$ , and the “goodness of fitting”,  $S$ , were used as numerical criteria for the quality of parameter fitting.

The definitions of “R-factors” and the “goodness of fitting”,  $S$ , were described in references [9,10]. To assure the convergence of the refined structural parameters, the refinements were carried out according to the following group orders: (1) scale factor, sample displacement and background; (2) cell parameters; (3) peak shape, half width and asymmetry parameter; (4) atomic position parameter (5) site occupancies and (6) isotropic thermal parameters.

### 3. RESULTS AND DISCUSSION

The XRD data were consistent with the orthorhombic structure with Pmmm symmetry for  $x=0.0$  and P4/mmm symmetry for  $x = 0.10, 0.15, 0.20, 0.25, 0.30$ . The Rietveld refinement technique was used to obtain the structural parameters. The  $c$ -axis increased with phosphate content, and the substitution of  $(\text{PO}_4)^{3-}$  at the Cu(1) site in  $[\text{Y,Ca}]\text{SrBaCu}_{3-x}(\text{PO}_4)_x\text{O}_y$  leads to a structural change from orthorhombic to tetragonal for  $x > 0$ .

Refined structural parameters were calculated for the orthorhombic phase from powder X-ray diffraction at room temperature for  $(\text{PO}_4)^{3-}$  doped YSBCPO samples.

The crystal structure has the Pmmm symmetry for  $x = 0.00$ . The atomic positions are: Y/Ca  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , Sr/Ba  $(\frac{1}{2}, \frac{1}{2}, z_{\text{Ba/Sr}})$ , Cu(1)  $(0,0,0)$ , Cu(2)  $(0,0,z_{\text{Cu(2)}})$ , O(1)  $(0, \frac{1}{2}, 0)$ , O(2)  $(\frac{1}{2}, 0, z_{\text{O(2)}})$ , O(3)  $(0, \frac{1}{2}, z_{\text{O(3)}})$  and O(4)  $(0,0,z_{\text{O(4)}})$ .

The refined structural parameters were calculated also for the tetragonal phase from powder X-ray diffraction at room temperature for  $(\text{PO}_4)^{3-}$  doped YSBCPO samples.

The crystal structure has the P4/mmm symmetry. The atomic positions are: Y/Ca  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , Sr/Ba  $(\frac{1}{2}, \frac{1}{2}, z_{\text{Ba/Sr}})$ , Cu(1)/P  $(0,0,0)$ , Cu(2)  $(0,0,z_{\text{Cu(2)}})$ , O(1)  $(0, \frac{1}{2}, 0)$ , O(2)  $(0,0,z_{\text{O(2)}})$ , O(3)  $(0,0,z_{\text{O(3)}})$ , O(4)  $(x_{\text{O(4)}}, y_{\text{O(4)}}, 0)$  and O(5)  $(0, y_{\text{O(5)}}, z_{\text{O(5)}})$ . The oxygens O(4) and O(5) were used to link the P atom. The occupancies of oxygen atoms located at O(1), O(4) and O(5) were refined with the refinements. But the occupancies of oxygen atoms located at O(4) and O(5) were inaccurate due to the weak X-ray scattering power for oxygen atoms. The structural parameters for the samples were refined so that the calculated pattern fits the observed one very well. A summary of the refined atomic parameters is given in table 1. The lattice parameters versus the  $(\text{PO}_4)^{3-}$  content,  $x$ , are plotted in figure 2 for all the samples studied.

The lattice parameter along the  $a$ -direction, first decreases with the  $(\text{PO}_4)^{3-}$  content and then stabilizes. The lattice parameter along the  $c$ -axis shows an initial increase with the  $(\text{PO}_4)^{3-}$  content followed by a subsequent decrease for higher  $(\text{PO}_4)^{3-}$  concentration. The jump may result from a loss of oxygen at the O(1) site which is compensated by  $\text{PO}_4$  doping leading to an increase of the total oxygen content in YSBCPO. The unit-cell volume dependence on  $x$  is shown in the figure 3. One sees that the unit-cell

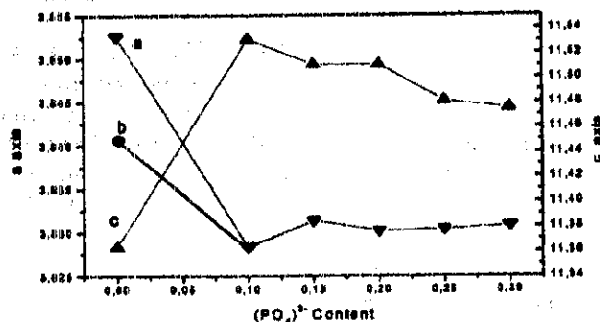


Figure 2. Lattice constants, *a* and *c* axis with  $(\text{PO}_4)^{3-}$  content

**Table 1.** Refined structural parameters for the orthorhombic phase from powder X-ray diffraction at room temperature for  $(\text{PO}_4)^{3-}$  doped YBCPO samples. The crystal structure has the Pmmm symmetry for  $x = 0.00$ . The atomic positions are: Y/Ca  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , Sr/Ba  $(\frac{1}{2}, \frac{1}{2}, z_{\text{Sr/Ba}})$ , Cu(1)  $(0, 0, 0)$ , Cu(2)  $(0, 0, z_{\text{Cu(2)}})$ , O(1)  $(0, \frac{1}{2}, 0)$ , O(2)  $(\frac{1}{2}, 0, z_{\text{O(2)}})$ , O(3)  $(0, \frac{1}{2}, z_{\text{O(3)}})$  and O(4)  $(0, 0, z_{\text{O(4)}})$  And the refined structural parameters for the tetragonal phase from powder X-ray diffraction at room temperature for  $(\text{PO}_4)^{3-}$  doped YBCPO samples. The crystal structure has the P4/mmm symmetry. The atomic positions are: Y/Ca  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , Sr/Ba  $(\frac{1}{2}, \frac{1}{2}, z_{\text{Sr/Ba}})$ , Cu(1)/P  $(0, 0, 0)$ , Cu(2)  $(0, 0, z_{\text{Cu(2)}})$ , O(1)  $(0, \frac{1}{2}, 0)$ , O(2)  $(0, 0, z_{\text{O(2)}})$ , O(3)  $(0, 0, z_{\text{O(3)}})$ , O(4)  $(x_{\text{O(4)}}, y_{\text{O(4)}}, 0)$  and O(5)  $(0, y_{\text{O(5)}}, z_{\text{O(5)}})$ .

$(\text{PO}_4)^{3-}$ Content (x)	0,00	0,10	0,15	0,20	0,25	0,30
A (Å)	3,8526	3,8283	3,8314	3,8302	3,8304	3,8308
B (Å)	3,8386					
C (Å)	11,3633	11,5310	11,5107	11,5106	11,4809	11,4751
$z_{\text{Sr}}$	0,17363	0,18605	0,18614	0,18618	0,18620	0,18604
$z_{\text{Ba}}$	0,17363	0,18605	0,18614	0,18618	0,18620	0,18604
$z_{\text{Cu(2)}}$	0,33880	0,35580	0,35540	0,35479	0,35424	0,35363
$z_{\text{O(2)}}$	0,33880	0,35580	0,35540	0,35479	0,35424	0,35363
$z_{\text{O(3)}}$	0,34855	0,18605	0,18614	0,18618	0,18620	0,18604
$x_{\text{O(4)}}$		0,38801	0,38657	0,38528	0,38637	0,38448
$y_{\text{O(4)}}$		0,16276	0,16271	0,16247	0,16236	0,16106
$y_{\text{O(4)}}$	0,17363					
$y_{\text{O(5)}}$		-0,15894	-0,15950	-0,16052	-0,15992	-0,16186
$z_{\text{O(5)}}$		0,15980	0,16017	0,16044	0,16016	0,16067
$T_c$ (K)	55,1	75,2	75,1	72,7	70,04	35,06
$\Delta T_c$ (K)	10,35	9,28	14,31	11,35	9,48	25,93
$R_p$ %	8,54	6,27	6,82	6,62	6,90	9,54
$R_{wp}$ %	12,11	8,41	9,47	9,21	9,33	14,19
S	2,74	1,88	2,12	2,08	2,08	3,13

volume that first increases, later decreases with increasing  $(\text{PO}_4)^{3-}$  content in YCSBCPO.

The substitution of Ca for Y should add holes to the Cu-O2 sheets (hole-doping or p-doping). If  $(\text{PO}_4)^{3-}$  substitution for Cu(1) at the Cu(1)-site produces electrons, then the addition of holes by replacing Y with Ca at the Y-site does not compensate the effect of  $(\text{PO}_4)^{3-}$  substituting for Cu(1) at Cu(1) site in

suppressing  $T_c$ . This behavior is observed in figure 4,  $T_c$  decreases with the increase of  $(\text{PO}_4)^{3-}$  concentration for  $x = 0.30$ . The transition width for each sample is listed in table 1.

The balance between p- (Ca substitution for Y) and n-doping ( $\text{PO}_4$  replacement for Cu(1)) will arrive at about  $x = 0.10$ , the over n-doped range in YCSBCPO corresponds to  $x > 0.10$ . With Ca over

doping in YCSBCPO, we guess that the occupancy of oxygen at the O(1) site decreases with the increase of  $(PO_4)^{3-}$  content in YCSBCPO with  $x > 0.10$ .

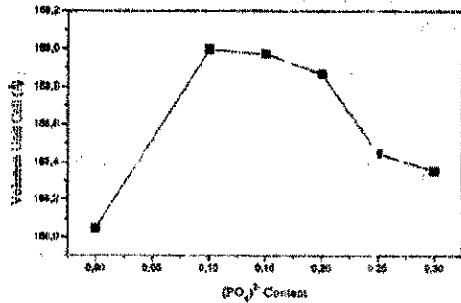


Figure 3. Unit-cell volume versus  $(PO_4)^{3-}$  content for  $[Y_{0.75}Ca_{0.25}]SrBaCu_{3-x}(PO_4)_xO_y$

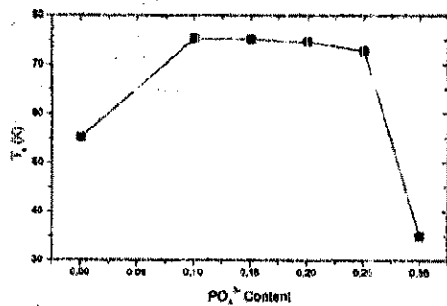


Figure 4. Dependence of the superconducting transition temperature  $T_c$  on the content of  $(PO_4)^{3-}$  for  $[Y_{0.75}Ca_{0.25}]SrBaCu_{3-x}(PO_4)_xO_y$

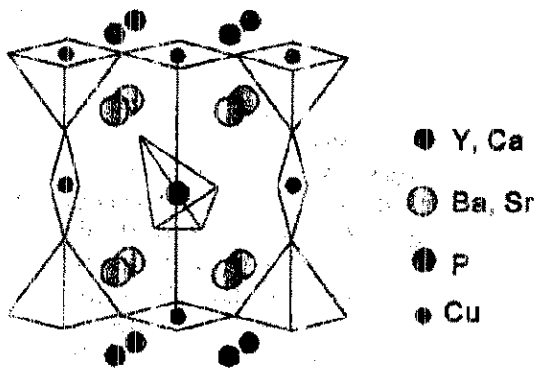


Figure 5. Schematic diagram of the possible structure of YCSBCPO.

The possible structure [3,11] of the phosphate derivatives of  $YBaSrCu_3O_7$  is one that contains some of the square planar  $CuO_4$  units along the Cu-O chains are replaced by the tetrahedral  $PO_4$  group.

Since  $[Y,Ca]SrBaCu_{3-x}(PO_4)_xO_y$  are superconducting, we have to conceive a structure which would not deplete the charge reservoir, wherein substitutions of the  $(PO_4)^{3-}$  group at the Cu(1) site creates both four and five coordination for Cu(2), as shown in figure 5, seem reasonable.

#### 4. ACKNOWLEDGMENTS

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