

STRUCTURAL REFINEMENT OF $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_y$

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ABSTRACT: $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_y$ samples with $0.10 \leq x \leq 0.40$ were synthesized using the solid state reaction technique. X-ray diffraction patterns show that all the compounds crystallized into a 123 tetragonal structure. The analysis of the structure with Rietveld refinement were made using a model that contains one Cu(2) in a four coordination and not in five coordination as in the other 123 tetragonal structures. This fact allows that T_c increase with Ca concentration. All samples are superconductors as reported in a previous paper.

Keywords: synthesis, Rietveld refinement, superconductivity, phosphate.

SUMILLA: Se sintetizaron muestras de $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_y$ con $0.10 \leq x \leq 0.40$ usando la técnica de reacción de estado sólido. Los patrones de difracción de rayos-x muestran que todos los compuestos cristalizaron en una estructura tetragonal 123. El análisis de la estructura con refinamiento de Rietveld, se hizo usando un modelo que contiene un Cu (2) en coordinación cuatro y no en cinco como en las otras estructuras tetragonales 123. Este hecho permite que T_c aumente con la concentración de Ca. Tal como se reportó en un artículo anterior, todas las muestras son superconductoras.

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

1. INTRODUCCIÓN

Cation doping in cuprates can produce lattice strain[1,2]. There are three effects on cuprates due to cation doping. One is the valence-induced carrier redistribution due to the differences in the valence and negative electricity between the dopants and the components. The second is the size effect resulting from the difference in the ionic radii between the dopant and the replaced component. The third one is the magnetic effect due to the difference in the magnetic moment between the dopants and the replaced components. Y substitution by Ca has been investigated by many research groups [3,4,5]. Since there is a difference in valence state (Ca^{2+} vs Y^{3+}) between the cations, the structure and the carrier concentration change with Ca content due to Ca^{2+} substituting Y^{3+} in YBCO [6,7]. The content of oxygen at the O(1) site decreases after Ca is added in YBCO. By studying the above results for Ca and PO_4 doped $YBaSrCu_3O_y$, compensations in the structural variation and carrier distribution are possible due to the opposite variations in valence and ionic radii between the local Y-site (Ca^{2+} substitution for Y^{3+}) and the local Cu(1)-site (PO_4 substitution for Cu(1)). In the present paper we report on the synthesis and X-ray characterization

of Ca and PO_4 co-doped $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_y$ (YCSBCPO) compounds.

2. EXPERIMENTAL PROCEDURES

The samples were prepared using the standard solid state reaction technique. The detailed procedures for sample preparation were described elsewhere [8]. 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 $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_y$ with $x = 0.10, 0.20, 0.25, 0.30, 0.40$. Each of these mixtures was ground for several tens of minutes. They were put into a furnace and annealed at $1000^\circ C$ in oxygen flow for about 16 hours. The resultant powders were reground and pelletized into disk-shaped pellets, and then put into the furnace 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 (ΔT_c) was defined as the width of the curve of the first derivative[9].

The diffraction data for the Rietveld analysis were collected at room temperature with a Rigaku powder diffractometer in the Bragg-Brentano

geometry. The data were collected over the diffraction range of 20-80°. A small amount of impurity phase was detected in our Ca and PO₄ codoped YCSBCPO samples. The collected diffraction patterns are shown in figure 1.

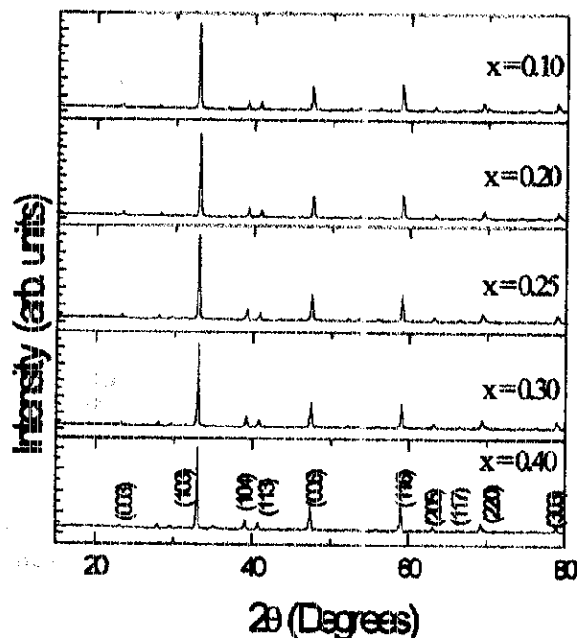


Figure 1. Powder X-ray diffraction patterns of $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_y$.

The standard analyzing program called 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 microabsorption corrections were applied to the raw data. The wavelengths of $CuK_{\alpha 1}$, $CuK_{\alpha 2}$ and the intensity ratio were 1,54050 Å; 1,54430 Å and 0,500, respectively.

The "goodness of fitting", S , was used as the numerical criteria for fitting. The definition of "goodness of fitting", S , was described in Ref. [10]. To assure convergence of the refined structural parameter, 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

All the samples were examined by powder X-ray diffraction. The X-ray diffraction data were analyzed in the tetragonal structure with $P4/mmm$ symmetry by the Rietveld refinement technique to obtain the structural parameters.

At the initial stage of refinement for the main phase of 123, it is assumed that the occupancies for the sites of Y ($1/2, 1/2, 1/2$), Ba ($1/2, 1/2, z_{Ba}$), Cu(1) (0,0,0), Cu(2) (0,0, z_{Cu}), O(2) (0,0, $z_{O(2)}$), O(3) (0,0, $z_{O(3)}$), are all set to 1.

Ca and Y were assumed to occupy the Y-site. PO₄ and Cu(1) were assumed to occupy the Cu(1)-site. Oxygen atoms were assumed to occupy the O(1), O(2), O(3), O(4) and O(5) sites. The oxygens O(4) and O(5) were used to link the P atom.

The occupancies of oxygen atoms at the O(1), O(4) and O(5) sites were refined during refinement. But the occupancies of oxygen atoms 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 Ca content, x curve, is plotted in figure 2 for YCSBCPO. The lattice parameter along the a -direction, first decreases up to $x = 0.25$ and then increases with Ca content.

The lattice parameter along the c -axis increases with Ca content (see figure 2).

The jump may result from a loss of oxygen at the O(1) site to compensate for PO₄ doping in YCSBCPO, the total oxygen content y will increase. As Ca is added, Ca usually occupies the Y-site in Ca-doped YBCO [7], the opposite valence effect occurred at the Y-site because Ca²⁺ has the larger ionic volume but lower valence state than those of Y³⁺. The charge valence reaches balance in YCSBCPO with $x = 0.25$ due to Ca and PO₄ codoping in YSBCO.

The larger Ca²⁺ ions that will replace for Y³⁺ ions [11], on the other hand, will induce local expanding stress around the Y-site.

The jumps of the lattice parameters will cause competition between these two local inner stresses.

With increasing Ca content in YCSBCPO, the unit-cell volume increases. The unit-cell volume dependence on x is shown in figure 3.

Table 1. Refined structural parameters for the tetragonal phase from powder X-ray diffraction data at room temperature for Ca doped YBCPO samples. The crystal structure has the $F4/mmm$ symmetry. The atomic positions are: Y/Ca ($1/2, 1/2, 1/2$), Sr/Ba ($1/2, 1/2, z_{Sr, Ba}$), Cu(1)/P ($0, 0, 0$), Cu(2) ($0, 0, z_{Cu(2)}$), O(1) ($0, 1/2, 0$), O(2) ($0, 0, z_{O(2)}$), O(3) ($0, 0, z_{O(3)}$), O(4) ($x_{O(4)}, y_{O(4)}, 0$) and O(5) ($0, y_{O(5)}, z_{O(5)}$).

Ca Content (x)	0.10	0.20	0.25	0.30	0.40
a (Å)	3,8349	3,8334	3,8312	3,8334	3,8351
c (Å)	11,4656	11,4783	11,5030	11,5020	11,5430
z_{Sr}	0,18607	0,18650	0,18677	0,18741	0,18932
z_{Ba}	0,18607	0,18650	0,18677	0,18741	0,18932
$z_{Cu(2)}$	0,35578	0,35410	0,35414	0,35692	0,35108
$z_{O(2)}$	0,35578	0,35410	0,35414	0,35692	0,35108
$z_{O(3)}$	0,18607	0,18650	0,18677	0,18741	0,18932
$x_{O(4)}$	0,38801	0,36928	0,38371	0,37745	0,37282
$y_{O(4)}$	0,16276	0,22005	0,22426	0,25037	0,16560
$y_{O(5)}$	-0,15894	-0,14227	-0,15080	-0,22928	-0,15461
$z_{O(5)}$	0,15980	0,12142	0,13301	0,11846	0,14675
T_c (K)	40,01	59,47	60,83	69,53	38,45
ΔT_c (K)	7,98	5,87	13,16	4,79	6,84
S	2,0	2,16	2,15	2,18	2,28

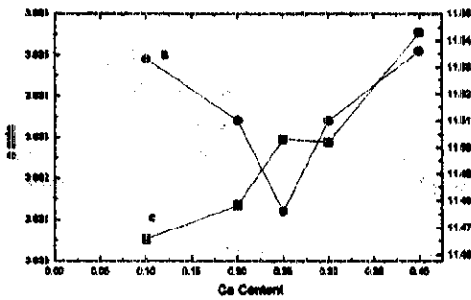


Figure 2. Lattice constants, *a* and *c* axis with Ca content.

The substitution of Ca for Y should add holes to Cu-O₂ sheets (hole-doping, or p-doping). If PO₄ substitution for Cu(1) at Cu(1)-site produces electrons, then the addition of holes by Ca replacing for Y at the Y-site should compensate the effect of PO₄ substituting for Cu(1) at the Cu(1) site in suppressing T_c.

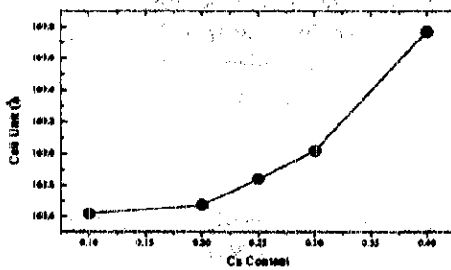


Figure 3. Unit-cell volume versus Ca content for $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_7$.

This behavior is observed in figure 4, T_c decreases with the increase of Ca concentration for x = 0.30. The transition width for each sample is listed in table 1.

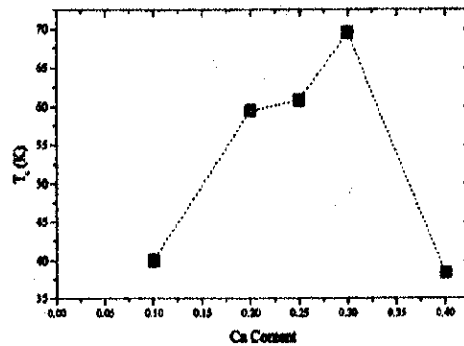


Figure 4. The superconducting transition temperature T_c dependence on the content of Ca for $[Y_{1-x}Ca_x]SrBaCu_{2.80}(PO_4)_{0.20}O_7$.

The balance between p- (Ca substitution for Y) and n-doping (PO₄ replacement for Cu(1)) will be reached at about x = 0.25, the over p-doped range in YCSBCPO corresponds to x > 0.25. With Ca over doping in YCSBCPO, we guess that the occupancy of oxygen at the O(1) site decreases with the increase of Ca content in YCSBCPO as x > 0.25.

The sample with x = 0.25 shows the maximum transition width, which may indicate that a large structural strain exists in the sample.

The occurrence of superconductivity in phosphate derivatives prepared under ambient conditions is noteworthy.

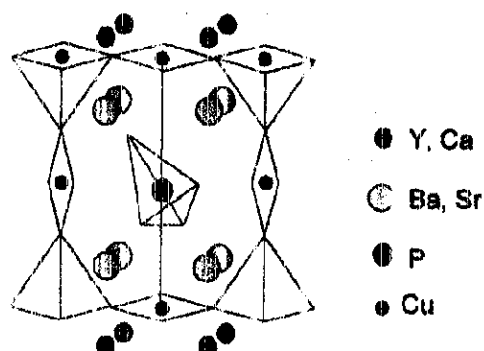


Figure 5. Schematic diagram of the possible Structure of YCSBCPO.

The possible structure[11,12,13] of the phosphate derivatives of $\text{YBaSrCu}_3\text{O}_7$ is that some of the square planar CuO_4 units along the Cu-O chains are replaced by the tetrahedral PO_4 group. Since $[\text{Y,Ca}]\text{SrBaCu}_{3-x}(\text{PO}_4)_x\text{O}_y$ 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 creating both four and five coordination for Cu(2) as shown in figure 5, seem reasonable.

4. ACKNOWLEDGEMENTS

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