STRUCTURAL ORDER AND PHASE FORMATION OF THE
SUPERCONDUCTOR LaCaBaCu$_2$X$_y$O$_{6.2}$ WITH X= (PO$_4$)$_3^-$ AND (BO$_3$)$_3^-$

Luis De Los Santos V.*, Dwight R. Acosta.*, Angel Bustamante D.*, Carlos R. Magaña*, Richard Bellido Q.*, Jesus Flores S.* and Andrés Díaz S.*

* Lab. Superconductividad, Facultad de Ciencias Físicas, Universidad Nacional Mayor de San Marcos

** Departamento Académico de Física, Facultad de Ciencias Naturales y Matemáticas, Universidad Nacional del Callao

| Instituto de Fisica. Universidad Nacional Autónoma de México

Abstract

The LaCaBaCu$_{2.4}$X$_{0.3}$O$_{6.8}$ compound with X= (PO$_4$)$_3^-$ and (BO$_3$)$_3^-$ has been prepared by a solid state reaction method and we compare the resulting structures, phase formation and Critical Temperatures ($T_c$s) with the well known LaCaBaCu$_2$O$_{7-\delta}$ (La1113) superconductor. For both cases, the X-ray diffractogram revealed the BaCuO$_2$ and CuO as extra phases; this is confirmed by SEM, EDX and HREM. The Rietveld analysis suggested orthorhombic crystalline structures belonging to the Pmmm spatial group with $a=3.849\,\AA$, $b=3.880\,\AA$ and $c=11.630\,\AA$ to the LaCaBaCu$_{2.4}$X$_{0.3}$O$_{6.8}$, $T_c$'s were calculated from the derivative of magnetic susceptibility plots by using a SQUID detection system, these indicated the $T_c$'s are 86K and 55K to the LaCaBaCu$_{2.4}$X$_{0.3}$O$_{6.8}$ and LaCaBaCu$_{2.6}$BO$_{3.2}$O$_{7-\delta}$ respectively. © 2006. All rights reserved

Keywords: Phosphate; Borate; Rietveld analysis; XRD.

I. INTRODUCTION

The literature reports that the LaCaBaCu$_2$O$_{6.9}$ (La1113) is one of the YBa$_2$Cu$_3$O$_{6.9}$-like superconducting compounds ($T_c$(onset) ~80K at $\gamma=6.87$) and isomorphous to tetragonal Y123 [1,2], with spatial group P4/mmm (a=b=3.8655Å and c=11.6354Å). Moreover it has been reported that La1113 can be stabilized by the incorporation of anions such as borate and phosphate [3-6]. In this work 0.2 of the both oxyanions phosphate (PO$_4$)$_3^-$ and borate (BO$_3$)$_3^-$ are replaced in the Cu site of La1113 structure. The LaCaBaCu$_{2.8}$X$_{0.2}$O$_{6.8}$ (La1113-X) with X= PO$_4$ and BO$_3$ were prepared to compare their structures and the phase formation with the well known LaCaBaCu$_2$O$_{6.8}$

II. EXPERIMENTAL

The samples were made by the conventional Solid State Reaction Method (SERM) and followed the same preparation done for the La1113 with PO$_4$ and BO$_3$. [4,5] Appropriate amounts of La$_2$O$_3$, BaCO$_3$, CaCO$_3$, CuO, NH$_4$H$_2$(PO$_4$) and H$_2$BO$_3$ were mixed and grinded in an Agata mortar to form pellets of 1cm diameter under 7 Ton per cm$^2$ pressure and followed by calcinations at 950°C for 24 h. Then the samples were reground and synthesized at 975°C in air for 12 h (60°C/h rate) before furnace cooling to room temperature. After grinding third time, the samples were annealed at 575°C in O$_2$ for 24 h and were furnace cooled to room temperature in the same gas atmosphere.

The X-ray powder data were collected between 20° and 80° with 0.02° step using a powder universal diffractometer, HGZ (Cu Kα radiation). The morphologic and EDX analysis were taken with the help of a Scanning Electron Microscope (SEM- Phillips XL30). High resolution electron microscopy observations were carried out in JEOL FEG 2010 microscope following standard procedures in order to detect nanostructured configurations. Finally, the magnetic susceptibilities, $\chi$ (T), were measured by
using a SQUID (Quantum Design) in Zero-Field Cooling (ZFC) process in an external field of 5 Oe, for temperatures between 5 and 100K.

III. RESULTS AND DISCUSSIONS

The room temperature XRD pattern of the La1113-PO₄ and La1113-BO₃ are shown in figure N° 1. Both cases reveal the presence of La1113-PO₄ and La1113-BO₃ as main phases respectively, and BaCuO₂ (represented in bold triangle) and CuO (represented in bold circle) as secondary phases. There are slightly differences between the main peaks of La1113-PO₄ and La1113-BO₃, these suggest some changes in the structure of La1113 under such anions substitution.

![XRD patterns of LaCaBaCu₄(PO₄)₂O₁₁ (top) and LaCaBaCu₄(BO₃)₂O₁₁ (middle) and LaCaBaCu₄O₁₁ (bottom)](image)

Fig 1. XRD patterns of LaCaBaCu₄(PO₄)₂O₁₁ (top) and LaCaBaCu₄(BO₃)₂O₁₁ (middle) and LaCaBaCu₄O₁₁ (bottom)

The structural model of La1113-PO₄ and La1113-BO₃ were refined by Rietveld analysis. We obtained the site occupancies of the cations from previous works [3,4], were orthorhombic crystalline structure belonging to the spatial group Pmmm were taken as models. The crystalline structure of La1113 is tetragonal belonging to the spacial group P4/mmm as found here and elsewhere [1,2]. Nevertheless, the occupancies of oxygen atoms sited at O(3), O(5) and O(6) were inaccurate due to the weak X-ray scattering power for oxygen atoms. The "goodness of fitting", S (the equivalent χ² used in statistical analysis for distributions), was used as the numerical of fitting. A summary of the refined atomic parameters is given in Table 1, were the volume of La1113's unit cell is 170.927 Å³; this volume increments 1.6% under the PO₄ substitution and 2.9% under BO₃ substitution.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>La1113</th>
<th>La1113-PO₄</th>
<th>La1113-BO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>3.849</td>
<td>3.849</td>
<td>3.884</td>
</tr>
<tr>
<td>b(Å)</td>
<td>3.849</td>
<td>3.88</td>
<td>3.89</td>
</tr>
<tr>
<td>c(Å)</td>
<td>11.537</td>
<td>11.53</td>
<td>11.64</td>
</tr>
<tr>
<td>Z_Ba</td>
<td>0.1844</td>
<td>0.181</td>
<td>0.175</td>
</tr>
<tr>
<td>Z_Ca(2)</td>
<td>0.1844</td>
<td>0.181</td>
<td>0.175</td>
</tr>
<tr>
<td>Z_O(2)</td>
<td>0.3732</td>
<td>0.3813</td>
<td>0.382</td>
</tr>
<tr>
<td>Z_O(3)</td>
<td>0.3773</td>
<td>0.3308</td>
<td>0.386</td>
</tr>
<tr>
<td>Z_O(4)</td>
<td>0.1584</td>
<td>0.1562</td>
<td>0.185</td>
</tr>
<tr>
<td>X_O(5)</td>
<td></td>
<td>0.2064</td>
<td>-0.05</td>
</tr>
<tr>
<td>Y_O(5)</td>
<td></td>
<td>-0.0188</td>
<td>0.4359</td>
</tr>
<tr>
<td>X_O(8)</td>
<td></td>
<td>0.3266</td>
<td>-0.08</td>
</tr>
<tr>
<td>Y_O(8)</td>
<td></td>
<td>0.4084</td>
<td>0</td>
</tr>
<tr>
<td>Z_O(6)</td>
<td></td>
<td>0.1323</td>
<td>0.2044</td>
</tr>
<tr>
<td>X_P</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Y_P</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>X₅</td>
<td></td>
<td>-0.0487</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1.17</td>
<td>1.9</td>
<td>1.91</td>
</tr>
</tbody>
</table>

According with Table 1, the oxyanions phosphate and borate enter nearly the Cu1 site in La1113's structure and create both four and five coordination at Cu2 site as shown in Fig 2 (a,b).

![Figure N° 2. Possible Incorporation of (a) phosphate and (b) borate into La1113 structure. As is shown the Oxianions occupy the Cu(1) site.](image)

The Scanning Electron Micrographs (SEM) for La1113-PO₄ with a zoom of 10000x is shown in Fig. 3, while SEM for La1113-BO₃ with a zoom of 10000x is shown in Fig. 4. In both cases significant changes of a normal heated
ceramic are not observed, but after Energy Dispersive X-ray analysis (EDX analysis), the chemical compose of each one are different.  

![Figure N° 3. Scanning electron micrograph of the LaCaBaCu_{2.5}(PO_{0.5})_{2.5}O_{6.2}](image)

![Figure N° 4. Scanning electron micrograph of the LaCaBaCu_{2.3}(BO_{0.5})_{2.5}O_{6.2}](image)

The EDX analysis of the samples (Fig 6-7), were done over the whole zones in the SEM micrographs shown above and using the secondary electron beams. The peak of Phosphorus (P) in Fig. 5 indicates its molecular weight about 2%, and the peak of Boron (B) in Fig. 6 indicates its molecular weight approximately 1.5%. The Au peaks are because samples were sprayed with Gold previously analysis.

Figure N° 7 shows HREM micrograph from sample LaCaBaCu_{2.5}(PO_{0.5})_{2.5}O_{6.2}, several grains presenting a nanostructured configuration can be observed. In the inset in the figure an electron diffraction pattern from the grain border is presented. In figure N° 8 the HREM micrograph from sample LaCaBaCu_{2.5}(BO_{0.5})_{2.5}O_{6.2} is shown, it can be observed a polytype configuration with periods close to 0.88 nm. Also some structural defects in the upper left side of the image are visible.

![Figure N° 5. EDX analysis of the LaCaBaCu_{2.5}(PO_{0.5})_{2.5}O_{6.2}](image)

![Figure N° 6. EDX analysis of the LaCaBaCu_{2.3}(BO_{0.5})_{2.5}O_{6.2}](image)

![Figure N° 7. HREM micrograph from sample LaCaBaCu_{2.5}(PO_{0.5})_{2.5}O_{6.2}](image)

Curves of Susceptibility (emu/mol) Vs. Temperature (K) are shown in Fig.9. Apparently susceptibility decays from 80K, 90K and 57 K. However, taking account the derivatives of the curves, as shown in the inset in the figure, we find that La1113,
La1113-PO$_4$ and La1113-BO$_4$ become superconductors at the Critical Temperatures 47K, 86K and 55K respectively. Nevertheless a minor uncertainty is present, particularly in the case of La1113-PO$_4$ because the presence of the secondary phases mentioned above.

**IV. CONCLUSION**

Phosphate (PO$_4$) and Borate (BO$_4$) enter nearly the Cu1 site into the LaCaBaCu$_4$O$_{7-\delta}$ structure, changing its structure from tetragonal P4/mmm to orthorhombic Pmmm, and creating both four and five coordination for Cu(2) as shown in Fig. 2; therefore we have to conceive of a structure which would change its charge reservoir permitting different $T_c$'s. The additional Oxygenes belonging to the Oxianions increase the number of the holes in the superconducting planes (CuO$_x$) in this way the respective $T_c$ change. From HREM images it can be derived the coexistence of different crystallographic phases in our samples. Finally, it is common to find BaCuO$_2$ and CuO as secondary phases since the sample preparation was following the solid state reaction method.

**V. ACKNOWLEDGEMENTS**

Luis De Los Santos thanks Dr. Juan Arroyo C from the Faculty of Chemistry & Chemical Engineering, San Marcos University and Prof. Carlos Quiñones M. from the Physics Department, University of Callao for their valuable comments.

**Figure N° 8.** HREM micrograph from sample LaCaBaCu$_{2x}$(BO$_{3.86}$)O$_{4.4}$

**Figure N° 9.** Susceptibility vs. temperature in ZFC for LaCaBaCu$_{4}$O$_{7-\delta}$ (La1113), LaCaBaCu$_{2x}$(PO$_{4.86}$)O$_{6.2}$ (La1113-PO$_4$) and LaCaBaCu$_{2x}$(BO$_{3.86}$)O$_{4.4}$ (La1113-BO$_4$).
VI. REFERENCES


