

## STRUCTURAL ORDER AND PHASE FORMATION OF THE SUPERCONDUCTOR $\text{LaCaBaCu}_{2.8}(\text{X})_{0.2}\text{O}_{7-\delta}$ WITH $\text{X} = (\text{PO}_4)^{3-}$ AND $(\text{BO}_3)^{3-}$

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### Abstract

The  $\text{LaCaBaCu}_{2.8}(\text{X})_{0.2}\text{O}_{7-\delta}$  compound with  $\text{X} = (\text{PO}_4)^{3-}$  and  $(\text{BO}_3)^{3-}$  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  $\text{LaCaBaCu}_3\text{O}_{7-\delta}$  (La1113) superconductor. For both cases, the X-ray diffractogram revealed the  $\text{BaCuO}_2$  and  $\text{CuO}$  as extra phases; this is confirmed by SEM, EDX and HREM. The Rietveld analysis suggested orthorhombic crystalline structures belonging to the Pmm spatial group with  $a=3.849\text{\AA}$ ,  $b=3.880\text{\AA}$  and  $c=11.630\text{\AA}$  to the  $\text{LaCaBaCu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_{7-\delta}$ , and  $a=3.884\text{\AA}$ ,  $b=3.890\text{\AA}$  and  $c=11.640\text{\AA}$  to the  $\text{LaCaBaCu}_{2.8}(\text{BO}_3)_{0.2}\text{O}_{7-\delta}$ .  $T_c$ '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  $\text{LaCaBaCu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_{7-\delta}$  and the  $\text{LaCaBaCu}_{2.8}(\text{BO}_3)_{0.2}\text{O}_{7-\delta}$  respectively. © 2006. All rights reserved

**Keywords:** Phosphate; Borate; Rietveld analysis; XRD.

### I. INTRODUCTION

The literature reports that the  $\text{LaCaBaCu}_3\text{O}_y$  (La1113) is one of the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (Y123)-like superconducting compounds ( $T_{c(\text{onset})} \gg 80\text{K}$  at  $y=6.87$ ) and isomorphic to tetragonal Y123 [1,2], with spatial group P4/mmm ( $a=b=3.8655\text{\AA}$  and  $c=11.6354\text{\AA}$ ). 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  $(\text{PO}_4)^{3-}$  and borate  $(\text{BO}_3)^{3-}$  are replaced in the Cu site of La1113 structure. The  $\text{LaCaBaCu}_{2.8}(\text{X})_{0.2}\text{O}_{7-\delta}$  (La1113-X) with  $\text{X} = \text{PO}_4$  and  $\text{BO}_3$  were prepared to compare their structures and the phase formation with the well known  $\text{LaCaBaCu}_3\text{O}_{7-\delta}$ .

### II. EXPERIMENTAL

The samples were made by the conventional Solid State Reaction Method (SERM) and followed the same preparation done for the La1113 with  $\text{PO}_4$  and  $\text{BO}_3$  [4,5] Appropriate amounts of  $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$ ,

$\text{NH}_4\text{H}_2(\text{PO}_4)$  and  $\text{H}_3\text{BO}_3$  were mixed and grinded in an Agata mortar to form pellets of 1cm diameter under 7 Ton per  $\text{cm}^2$  pressure and followed by calcinations at  $950^\circ\text{C}$  for 24 h. Then the samples were regrind and synthesized at  $975^\circ\text{C}$  in air for 12 h ( $60^\circ\text{C/h}$  rate) before furnace cooling to room temperature. After grinding third time, the samples were annealed at  $575^\circ\text{C}$  in  $\text{O}_2$  for 24 h and were furnace cooled to room temperature in the same gas atmosphere.

The X-ray powder data were collected between  $20^\circ$  and  $80^\circ$  with  $0.02^\circ$  step using a powder universal diffractometer, HGZ (Cu K $\alpha$  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-PO<sub>4</sub> and La1113-BO<sub>3</sub> are shown in figure N° 1. Both cases reveal the presence of La1113-PO<sub>4</sub> and La1113-BO<sub>3</sub> as main phases respectively, and BaCuO<sub>2</sub> (represented in bold triangle) and CuO (represented in bold circle) as secondary phases. There are slightly differences between the main peaks of La1113-PO<sub>4</sub> and La1113-BO<sub>3</sub>, these suggest some changes in the structure of La1113 under such anions substitution.

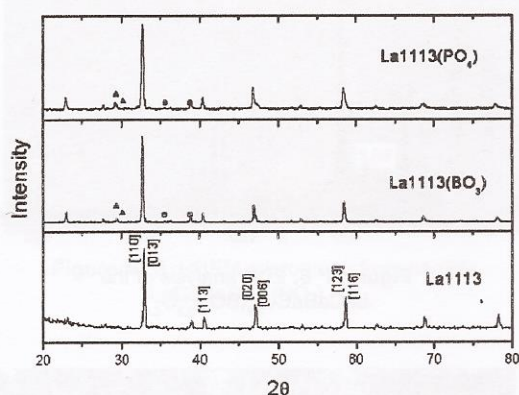


Fig 1. XRD patterns of LaCaBaCu<sub>2.8</sub>(PO<sub>4</sub>)<sub>0.2</sub>O<sub>6.2</sub> (top) and LaCaBaCu<sub>2.8</sub>(BO<sub>3</sub>)<sub>0.2</sub>O<sub>6.4</sub> (middle) and LaCaBaCu<sub>3</sub>O<sub>7-δ</sub> (bottom)

The structural model of La1113-PO<sub>4</sub> and La1113-BO<sub>3</sub> 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  $\chi^2$  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 Å<sup>3</sup>; this volume increments 1.6% under the PO<sub>4</sub> substitution and 2.9% under BO<sub>3</sub> substitution.

Table 1. Refined structural parameters for the LaCaBaCu<sub>3</sub>O<sub>7-δ</sub> (P4/mmm spatial group), LaCaBaCu<sub>2.8</sub>(PO<sub>4</sub>)<sub>0.2</sub>O<sub>6.2</sub> and LaCaBaCu<sub>2.8</sub>(BO<sub>3</sub>)<sub>0.2</sub>O<sub>6.4</sub> (Pmmm spatial group) from X-ray diffraction at room temperature.

Parameter.	La1113	La1113-PO <sub>4</sub>	La1113-BO <sub>3</sub>
a(Å)	3.849	3.849	3.884
b(Å)	3.849	3.88	3.89
c(Å)	11.5375	11.63	11.64
Z <sub>Ba</sub>	0.1844	0.181	0.175
Z <sub>Ca(2)</sub>	0.1844	0.181	0.175
Z <sub>O(2)</sub>	0.3732	0.3813	0.382
Z <sub>O(3)</sub>	0.3773	0.3308	0.386
Z <sub>O(ap)</sub>	0.1584	0.1562	0.185
X <sub>O(5)</sub>	—	0.2064	-0.05
Y <sub>O(5)</sub>	—	-0.0188	0.4359
X <sub>O(6)</sub>	—	0.3266	-0.08
Y <sub>O(6)</sub>	—	0.4084	0
Z <sub>O(6)</sub>	—	0.1323	0.2044
X <sub>P</sub>	—	0.2	—
Y <sub>P</sub>	—	0.2	—
X <sub>B</sub>	—	—	-0.0487
S	1.17	1.9	1.91

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).

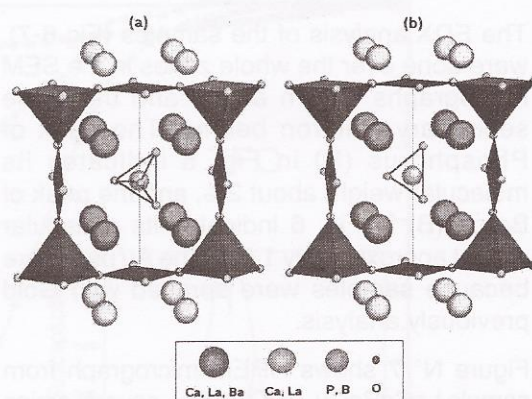


Figure N° 2. Possible incorporation of (a) phosphate and (b) borate into La1113 structure. As it is shown the Oxyanions occupy the Cu(1) site.

The Scanning Electron Micrographs (SEM) for La1113-PO<sub>4</sub> with a zoom of 10000x is shown in Fig. 3, while SEM for La1113-BO<sub>3</sub> 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.

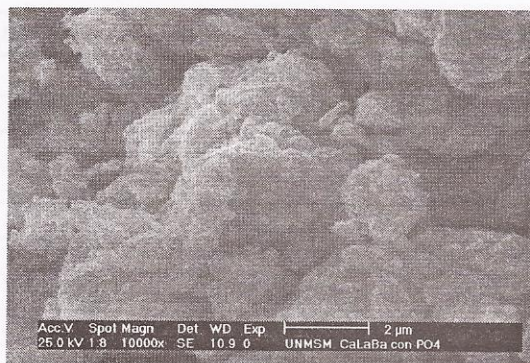


Figure N° 3. Scanning electron micrograph of the  $\text{LaCaBaCu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_{6.2}$ .

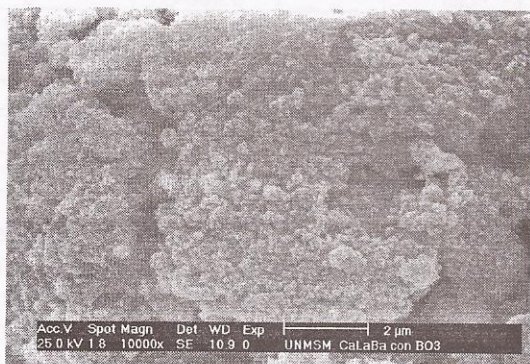


Figure N° 4. Scanning electron micrograph of the  $\text{LaCaBaCu}_{2.8}(\text{BO}_3)_{0.2}\text{O}_{6.4}$ .

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  $\text{LaCaBaCu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_{6.2}$ , 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  $\text{LaCaBaCu}_{2.8}(\text{BO}_3)_{0.2}\text{O}_{6.4}$  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.

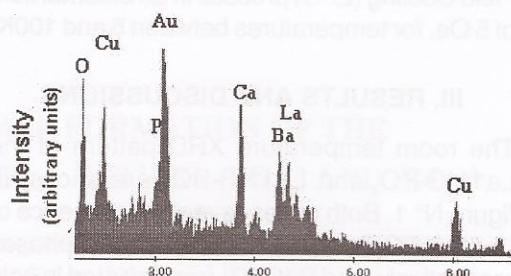


Figure N° 5. EDX analysis of the  $\text{LaCaBaCu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_{6.2}$ .

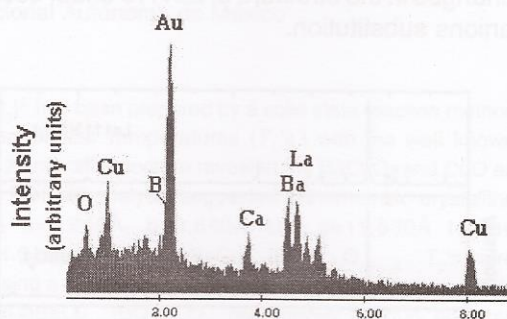


Figure N° 6. EDX analysis of the  $\text{LaCaBaCu}_{2.8}(\text{BO}_3)_{0.2}\text{O}_{6.4}$ .

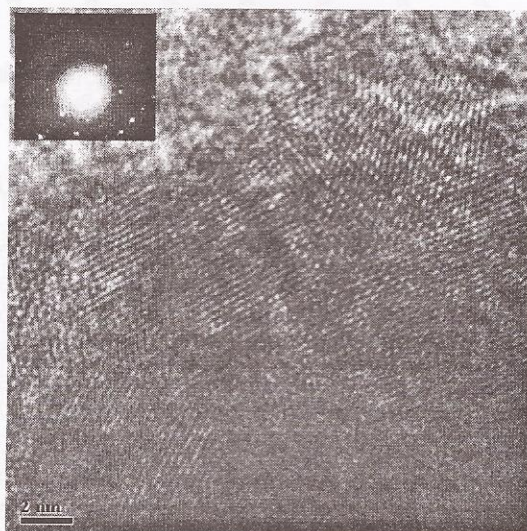


Figure N° 7. HREM micrograph from sample  $\text{LaCaBaCu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_{6.2}$ .

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<sub>4</sub> and La1113-BO<sub>3</sub> become superconductors at the Critical Temperatures 47K, 86K and 55K respectively. Nevertheless a minor uncertainty is present, particularly in the case of La1113-PO<sub>4</sub> because the presence of the secondary phases mentioned above.

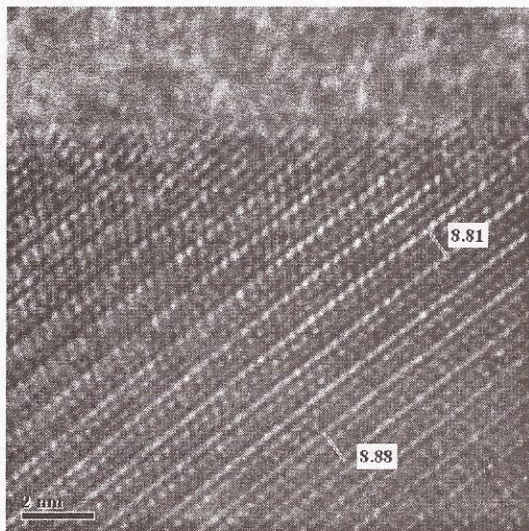


Figure N° 8. HREM micrograph from sample LaCaBaCu<sub>2.8</sub>(BO<sub>3</sub>)<sub>0.2</sub>O<sub>6.4</sub>

#### IV. CONCLUSION

Phosphate (PO<sub>4</sub>) and Borate (BO<sub>3</sub>) enter nearly the Cu1 site into the LaCaBaCu<sub>3</sub>O<sub>7-δ</sub> 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<sub>c</sub>'s. The additional Oxygens belonging to the Oxianions increase the number of the holes in the superconducting planes (CuO<sub>2</sub>) in this way the respective T<sub>c</sub>s change. From HREM images it can be derived the coexistence of different crystallographic phases in our samples. Finally, it is common to find BaCuO<sub>2</sub> and CuO as secondary phases since the sample preparation was following the solid state reaction method.

#### V. ACKNOWLEDGEMENTS

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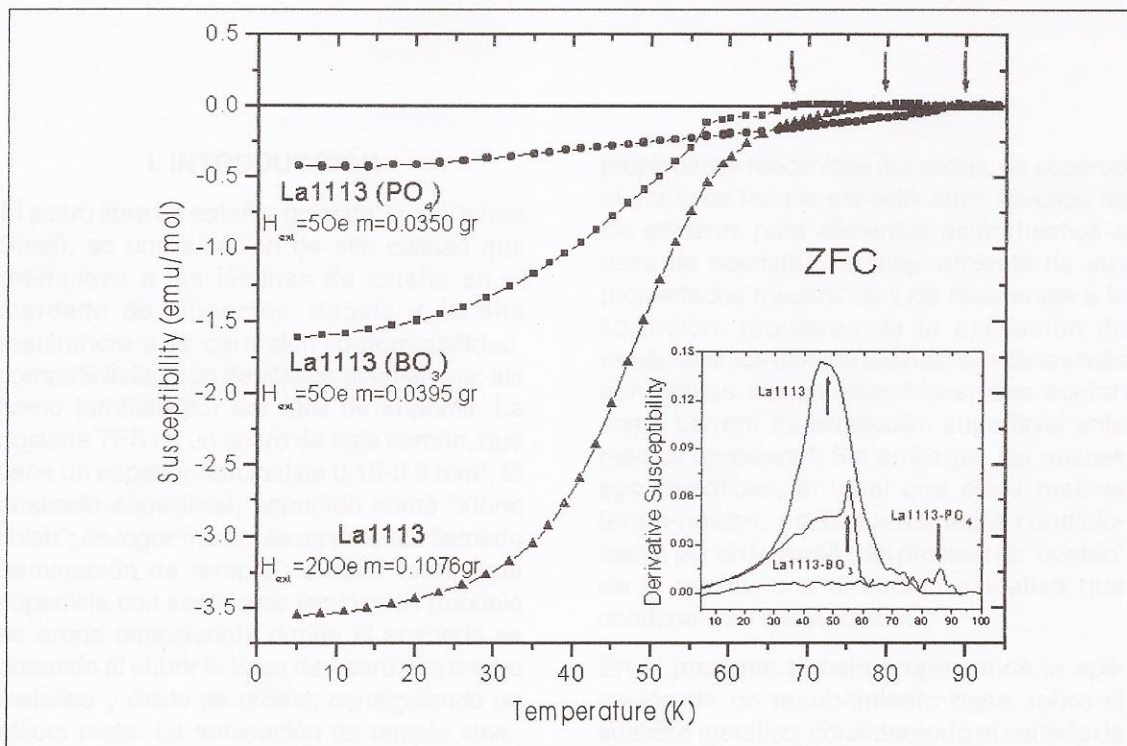


Figure N° 9. Susceptibility vs. temperature in ZFC for LaCaBaCu<sub>3</sub>O<sub>7-δ</sub> (La1113), LaCaBaCu<sub>2.8</sub>(PO<sub>4</sub>)<sub>0.2</sub>O<sub>6.2</sub> (La1113-PO<sub>4</sub>) and LaCaBaCu<sub>2.8</sub>(BO<sub>3</sub>)<sub>0.2</sub>O<sub>6.4</sub> (La1113-BO<sub>3</sub>).

## VI. REFERENCES

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