Conf-910736--5
SAND--91-0773C

SUPERCONDUCTING SUPEROXYGENATED $La_{2-x}Sr_xCuO_{4+\delta}$:SEARCH FOR PHASE SEPARATION

DE91 015334

B. Morosin*, G. H. Kwei**, J. E. Schirber*, J. A. Voigt*, E. L. Venturini* and J. A. Goldstone**

*Sandia National Laboratories, Albuquerque, NM 87185, **Los Alamos National Laboratory, Los Alamos, NM 87545

High pressure (2.3 kbar) high temperature (575°C) oxygen annealed ceramic $La_{2-x}Sr_xCuO_{4+\delta}$, with x=0.1 and 0.16, have been studied by high-resolution neutron powder diffraction to determine their low temperature structural properties in comparison to similarly oxygenated $La_2CuO_{4+\delta}$. Unlike $La_2CuO_{4+\delta}$, these Sr-containing superconductors show no low temperature phase separation. Further, for x= 0.16, the interstitial oxygen appears to be located at (1/4, 1/4, z) with z=0.163(5) and to have a value of δ consistent with $La_{1.84}Sr_{0.16}CuO_{4.019}$. Such a site is significantly displaced away from the interstitial location, (1/4, 1/4, z) with z ≃ 0.25 observed in $La_2CuO_{4+\delta}$. For x= 0.1, no interstitial oxygen is found and δ = 0.0.

1. INTRODUCTION, RESULTS, AND DISCUSSION

The presence of excess interstitial oxygen in $La_2CuO_{4+\delta}$ has been shown to result in a complex behavior upon cooling which involves a phase separation[1]. Since reported broadening of the (400) and (040) peaks in $La_{2-x}Sr_xCuO_{4+\delta}$[2] at low temperatures is consistent with results in $La_2CuO_{4+\delta}$, detailed structure refinements were performed for the Sr-containing alloys. Meissner data were obtained on chemical precipitated (1100° sinter) samples at various processing steps. Of particular interest is the increase in T_c from 38.0 to 39.5 K for x=0.16 upon oxygenation under 2.3 kbar at 575°C, such a difference was not observed for x=0.1 (T_c=31.9 K).

High-resolution TOF neutron powder diffraction data were collected at various temperatures between 295 and 15 K. The neutron data showed that both x=0.10 and 0.16 samples are single phase at all sample temperatures studied; these super-oxygenated materials did not exhibit phase separation into stoichiometric and oxygen rich phases as does $La_2CuO_{4+\delta}$.[1] At room temperature, all peaks were indexed to the space group F4/mmm while at lower temperatures, as expected from the tetragonal to orthorhombic phase transformation, many peaks split and the diffraction patterns were completely indexed with one cell of space group Bmab. However, annealing in high pressure oxygen does produce some changes in the details of the x = 0.16 structure which are easily observed by comparing the lattice constants for the materials. *c/a* is slightly larger and the low-temperature orthorhombic distortion *(b-a)/(b+a)* decreases for the super-oxygenated materials. A similar behavior is found for $La_2CuO_{4+\delta}$ relative to stoichiometric La_2CuO_4.[1]

In these Rietveld refinements, the atomic positions and thermal parameters for La and Sr were constrained to be the same; their occupancies were set at the expected stoichiometry and not refined. Parallel refinements with occupancy factors for the lattice oxygen atoms were also carried out. Values equal to 1.0 (within several estimated standard deviations, esd's), with those for the apical O2 slightly greater than the planar O1, were obtained indicating no oxygen vacancies were present.

Since the high pressure oxygen anneal increases T_c by 1.5 K in the x=0.16 sample, we also explored the possibility that charged oxygen defects like those in $La_2CuO_{4+\delta}$[1] may be incorporated. Refinement is more difficult because of the even lower occupancy of the

eb

---

oxygen defect. Initially an oxygen, O3, was placed with a small occupancy at the (1/4, 1/4, 0.23) site found in $La_2CuO_{4+\delta}$.[1] This failed to properly refine. A difference fourier synthesis showed small nuclear scattering peaks at the (1/4, 1/4, 0.16) site as well as at several other physically unreasonable sites. Placing O3 at the (1/4, 1/4, 0.16) site, refining first the position and then the occupancy, with a fixed isotropic thermal parameter (estimated value appropriate for the sample temperature), yielded stable refinements with an average value for the five different temperature data sets corresponding to $\delta = 0.019$ at a position near $z = 0.163$. This places the extra oxygen defect at a different location along z from that found in $La_2CuO_{4+\delta}$[1] and gives a stoichiometry $La_{1.84}Sr_{0.16}CuO_{4.019}$.

The parallel refinement on data for x=0.10 yielded occupancy factors for the interstitial oxygen which were usually negative, but effectively zero within several esd's. The occupancy factors for the lattice oxygens are equal to 1.0 (again within several esd's).

The location of the interstitial oxygen is quite different in $La_{1.84}Sr_{0.16}CuO_{4.019}$ (z=0.163) compared with the value determined in $La_2CuO_{4.032}$ (z=0.242); the latter value is quite close to the T′ position and at the largest vacant space in the crystal (at z=0.25). Thus the nature of the interstitial oxygen is very different in the Sr-doped material. This hypothesis is strengthened when the interatomic separations are considered for this defect.

2. CONCLUDING REMARKS

At 295 K, the location of the interstitial site is 1.905(8)Å from two O2 ions and 1.912(9)Å from two La/Sr ions with the next closest contact being O1 at 2.15(6)Å. This unusual environment with short separations may be only consistent with a neutral oxygen atom (radius ~0.66Å). Since the 1.20Å value for the ionic radius of La^{3+} is about 0.07Å shorter than the 1.27Å value for Sr^{2+}, it is very likely the interstitial oxygen will favor sites whose neighbors are filled with La^{3+} ions. This very different disposition of the defects may also be responsible for the lack of a phase separation upon cooling for this material compared to $La_2CuO_{4+\delta}$. The La^{3+} act as traps for the defects in the presence of Sr^{2+} ions and this prevents the diffusion of oxygen required to achieve phase separation.

The significantly higher T_c (39.5K) for oxygenated $La_{1.84}Sr_{0.16}CuO_{4.019}$ than for $La_{1.84}Sr_{0.16}CuO_4$ (38.0K) is intriguing. If the additional oxygen were simply adding or removing carriers (holes) to achieve optimal doping, one would expect a higher T_c in our x=0.18 (36.5(5) K) or x=0.14 (38.0(5) K) samples, which is not observed. Hence, the increase in T_c for x=0.16 upon oxygenation is most likely due to the dramatic reduction in orthorhombicity at low temperature rather than a beneficial change in carrier concentration and is consistent with the structural evidence for neutral interstitial oxygen, emphasizing the extreme sensitivity of superconductivity in this system to symmetry and local lattice distortions.

ACKNOWLEDGEMENTS

Supported by DOE contracts W-7405-ENG-36 (LNL) and DE-AC04-76DP00789 (SNL) as well as personnel at LANSCE (LNL) and IPNS (Argonne).

REFERENCES

1. J.D. Jorgensen, et al., Phys. Rev. B38 11337 (1988); C. Chaillout, et al., Physica C158 183 (1989); C170 87 (1990).

2. P. Day, et al., J. Phys. C20 L429 (1987).