مجله بلورشناسی و کانی‌شناسی ایران
شمارهٔ ۱، بهار و تابستان۸۶، از صفحهٔ ۲۴۳ تا ۲۵۰

مطالعه فاز مخلوط ساختاری بوسیله پراش از نمونه‌های پودری $YBa_2Cu_3O_{6+x}$ در دماهای ۲۰۰ °C و ۳۰۰ °C

بهرام خوشنویسان[۱]، د. ک. راس[۲]

۱ - گروه فیزیک- دانشگاه کاشان- ایران.
۲- انستیتو پژوهشی مواد - دانشگاه سالفورد - انگلستان.

(دریافت مقاله ۱۳۸۵/۸/۱۰ ، دریافت نسخه نهایی ۱۳۸۶/۲/۹)

چکیده: در این پژوهش اثر اکسیژن‌دهی بر نمونه‌های $YBa_2Cu_3O_{6+x}$ در دماهای ۲۰۰ °C و ۳۰۰ °C بررسی شده است. نتایج نشان می‌دهندکه نمونه‌ها با جذب اکسیژن و درنتیجه تغییر در مقدار موازنهٔ اتمی اکسیژن (که با مقدار x مشخص شده است) از فاز تتراگونال (T) به فاز مخلوط T+OII، که (OII) یک فاز ابر ساختاری ارتورمبیک است تغییر ساختار می‌دهند. دیده می‌شود با افزایش تدریجی مقدارx، درصد حضور فاز OII در مخلوط به صورت خطی افزایش یافته که البته این خود مؤید تبعیت انتقال فاز ازT به OII از قانون "انتقال فاز گیبس" بوده و لذا این انتقال فاز از نوع مرتبه اول است. حضور یک فاز پایدار OII که برای موازنهٔ اتمی اکسیژن در حدود x≈۰/۷ و در دمای ۳۰۰ °C توسط برون یابی پیش‌بینی می‌گردد می‌تواند یک اصلاح قابل توجه در نمودار فازهای ساختاری YBCO به وجود آورد. از مطالعه و تحلیل داده‌ها با استفاده از روش "ریتولد" نمی‌توان احتمال تشکیل یک ابرساختار در راستای c را منتفی دانست زیرا تاثیر مرزهای نا همفاز در پهن شده‌گی بازتابهای [00l] محتمل است. با اعمال عامل ساختاری "ابرساختار OII" مطالعه کمی فاز OII امکان پذیر شد.

واژه‌های کلیدی: *ارتورمبیک – ابرساختار.*

No. 1, 1386/2007 Spring & Summer

An in situ powder diffraction study of the structural mixed-phase of $YBa_2Cu_3O_{6+x}$ at 200 and 300°C

B. Khoshnevisan[1], D. K. Ross[2]

1. University of Kashan, Kashan, Iran
2. Institute for Materials Research, University of Salford, UK
Email:b.khosh@kashanu.ac.ir

(Received: 1/11/2006, received in revised form:29/4/2007)

Abstract: In this study, the $YBa_2Cu_3O_{6+x}$ samples at temperatures 200 and 300°C, as the value of x (the oxygen content in 0the basal plane) increased under nearly thermodynamical equilibrium condition, the structure changed from the well- known tetragonal (T) to a mixed-phase (T+OII) region (orthorhombicII phase is a superstructure). This mixed-phase region suggests a first order T/OII phase transition with the expected linear change in the volume fraction of each phase (phase lever rule). The existence of a stable whole OII phase region around $x \approx 0.7$ at 300°C, which is indicated by extrapolation, implies a substantial correction on the YBCO's structural phase diagram. From the full analyses of the data by Reitveld Method, the possibility of the formation of another superstructure along the c direction can not be ruled out (broadening of [00l] reflections which, presumably comes from anti phase boundary effects). By inserting the structure factor of the OII phase, we have been able to study this phase quantitatively.

Keywords: *orthorhombic II, superstructure, YBCO.*

1) Introduction

A large number of studies on YBCO ($YBa_2 Cu_3 O_{6+x}$ where $0<x<1$) have been carried out to elucidate the microstructures caused by the dynamical changes of the oxygen content in this H-T_c superconductor (normal state). Despite the extensive previous works on this topic, there is a very few investigations have been performed on the phase structure in the lower range of temperature (200 & 300°C) because of the relatively sluggish oxygen dynamics.

In this range, according to previous reports [1,2,3], YBCO is stable in three structural phases (depending on the oxygen content, x), tetragonal (T), orthorhombic (OI) and the superstructural orthorhombicII (OII) phase. In the tetragonal phase ($x<0.2$), the short O-Cu-O chains form in both a and b directions in the basal plane (tweed patterns) in order to maintain the four-fold symmetry of the unit cell around the c axis in average.

The concatenated long chains along the b direction characterize the OI phase whereas in the OII phase chains form in that direction in every other column. Starting from the tetragonal phase by adjusting the ambient oxygen partial pressure (PO2), so changing the oxygen stoichiometry (x), in an isothermal in situ process, it is possible to enter the other phases directly or through an intermediate mixed-phase region and vice versa, depending on whether the phase transition is second or first order. It should be stressed that the question of the first or second order characteristic of the phase transition at low and elevated temperature (<450ºC) regions has been a very controversial issue to date [3].

During in situ XRD or neutron diffraction (ND) measurements to study the T/OII phase transitions, we have noticed that some new reflections has been appeared along with the anisotropic peak broadening process. Obviously the creation of new peaks indicates the presence of a new phase, whereas the broadening of the diffraction peaks is mainly due to the intrinsic crystal defects such as micro strains and crystallite or particle size effects [4].

2) Experimental procedure

The powder sample used in this work was prepared with high purity and high stoichiometry ($x> 0.99$), i.e.YBa2Cu3O 6.99 (in the OI phase), and the particle size range was 1-5 μm. The in situ XRD measurements have been performed in a sample environment chamber that operates up to 300°C and the PO_2 could be controlled up to 1 bar manually (D5000, SIEMENS).

Because the oxygen diffusion process is rather slow, before each measurement the sample had to be left for several hours under the desired

PO_2 to allow oxygen atoms diffuse into the sample particles. The range of pressure variation was between 0.07 and 1000 mbar. Data collection lasted about 6 hours at each isobaric step and then the sample was cooled quickly to the ambient temperature. The reproducibility of data from repeated measurements shows that no change in the oxygen stoichiometry results from the thermal cycling [3]. The sample was taken to the tetragonal phase first by out gassing under vacuum (0.01 mbar) at 650°C for at least 3 hours so that the oxygen content was less than 6.20, (x< 0.20). Here the [010] and [020] peaks have been completely merged to the [100] and [200] peaks, that shows the main feature of transition to tetragonal phase. Then the sample dosed up to cross the phase boundaries by changing the ambient PO_2 under an isothermal procedure.

Because thermal neutrons are more sensitive to light atoms such as oxygen, an extensive series of neutron diffraction (ND) measurements have been carried out using D1A diffractometer at the Institute Laue-Langevin (ILL); France.

3) XRD in-situ measurements

Figs. 1(a-b) show a clear modifications in the x-ray diffraction patterns as a function of PO_2 (or the x values) at 200ºC. A room temperature pattern from a pre-prepared sample with x~0.2 (T Phase) has been attached just as a reference. The new peaks have shown with prefix 'S' among the matrix tetragonal phase peaks (prefix 'T') after oxygen up taking. These absorbed oxygen atoms in turns, create the local strain fields which lead to the broadening of the initial phase peaks. More investigations using whole profile refinement, GSAS, suggests the coexistence of a mixed phase (T+OII) region in here. The position of the [S.006] peak indicates that the average c_{OII} parameter is less than c_T, in agreement with the expected unit cell's contraction in the c direction with increasing the concentration of the ordered oxygen atoms in the basal plane [5]. The noticeable point is the reduction of the intensity of the 'T' peaks against the increasing intensity trend of the OII peaks (the 'S' peaks) whereas, the slight shifts are due to the changing of the lattice parameters after oxygen absorption. It should be noted that [S.213] is a clear indication of OII phase, i.e. there is no equivalent line from the tetragonal lattice (it would be indexed 2, 1/2, 3 on the original lattice unit cell).

4) Neutron diffraction (ND) at 200 and 300°C

Since the oxygen diffusion process at less than 450°C is very slow and the available neutron beam time was very limited, a series of predetermined oxygen contain samples with x ≈ 0.2, 0.3, 0.4 and 0.6 have been prepared.

For the ND measurements samples were loaded into a sealed Vanadium tube in the furnace and before the main data collection at each step two quick 45 minute runs were performed to ensure the stability of the diffraction pattern of the samples.

In Fig.2 the growth of a superlattice peak [S.102] with increasing oxygen content is noticeable and the growing of the OII phase with increasing x is consistent with the XRD results. On the other hand, this peak is important because there is no tetragonal phase peak in this relatively high d-spacing range.

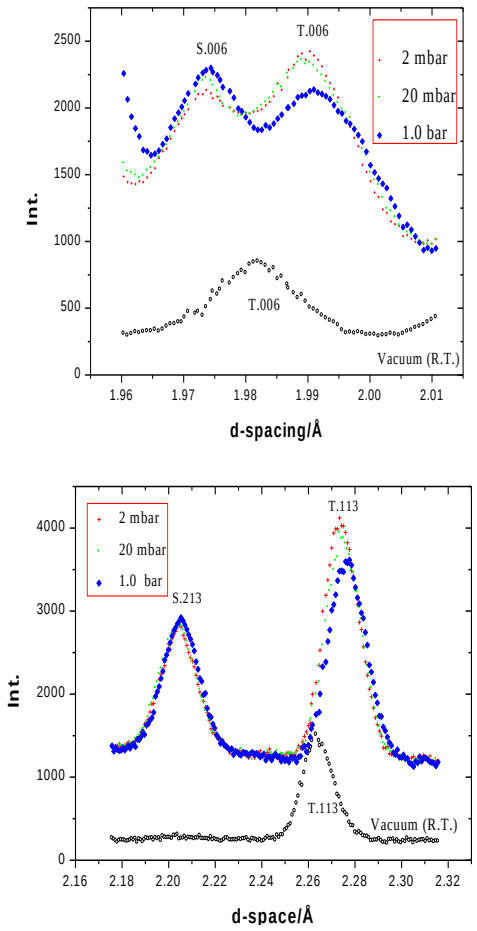

Fig 1 L) Growth of the OII peak [S.006], against the tetragonal peak [T.006], R) Sluggish growth of the OII peak [S.213], against the tetragonal peak [T.113] with increasing PO_2 at 200ºC. The vacuum (R.T.) indicates an entirely tetragonal [T.006] peak at room temperature (XRD data).

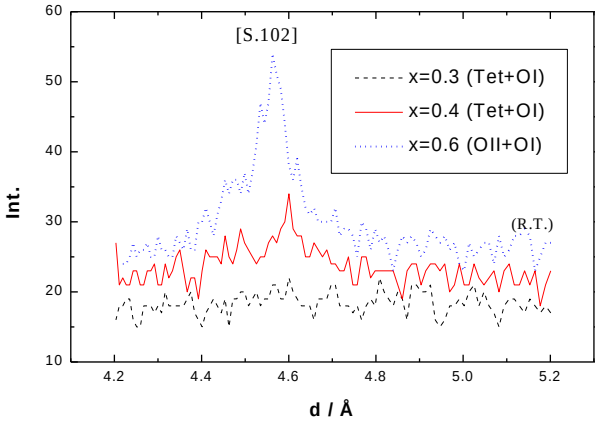

Fig 2 Growth of OII [102] peak with increasing oxygen content at 300˚C. The data at x≈0.6 was collected at room temperature (Neutron data).

5) Profile refinements of the neutron data

For the Reitveld Method profile refinement a mixed-phase (T+OII) model has been employed and some of the results are presented in table 1. As the table shows, the quality of refinements deteriorated with increasing the values of x.

All the refinements are subjected to a number of factors:

a_ The lack of a rational model for the tetragonal tweed structure in the tetragonal phase. This corresponds to a random clustering of ordered oxygen occupancy along a or b directions in the basal plane that makes its modeling very difficult.

b_ Large broadening of the [00l] reflections in the OII phase, as indicated by the arrows in Fig.3, which increased with the OII phase volume fraction. The main reason for this effect could be forming of "anti-phase boundaries" between adjacent layers along the c direction [6].

The arrows show the very broad [00l] lines for the OII phase. The upper and lower toggles are for OII and T phases.

c_ The other possibility that cannot be ruled out is the presence of some kind of periodic structure among a few unit cells along the c direction that leads to a modulation around [00l] reflections [7, 8].

Despite the above factors which create to some extent uncertainty in the quantities extracted from the profile refinement, the general trend of the measurements is in agreement with the expected mixed-phase region behaviour like the lever rule, Fig.4.

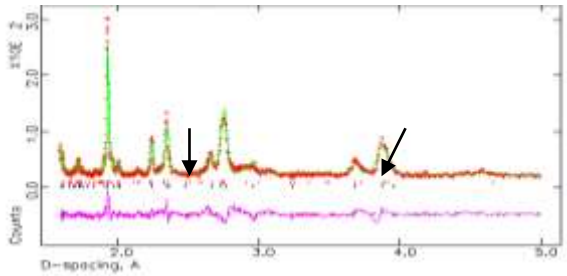

Fig 3 The neutron diffraction of the sample with x~ 0.4 at 300 ºC. χ^2 = 12.85 and R_p = 0.106.

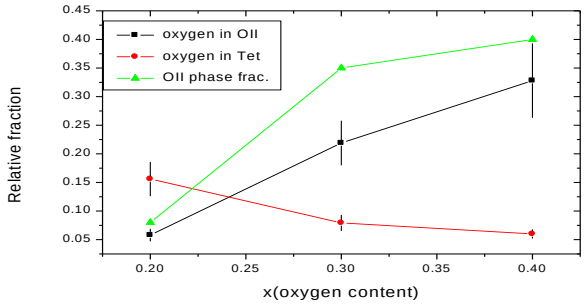

Fig 4 The relative OII phase fraction vs. x at 300˚C (error bars included).

Conclusion

The character of the YBCO's mixed-phase (T+OII) at elevated temperature (200-300°C) has been studied by powder in situ XRD and ND measurements. The popular ASYNNNI lattice-gas model which has successfully explained the majority of the high-temperature features of the YBCO's structural phase diagram here predicts a second order T/OII phase transition , consistent with a Screened Coulomb repulsion potential [9] model, but the other calculations based on the "de Fontaine" model [10] predict a first order transition. In this study we have presented some strong experimental evidences in favor of the first order transition scenario. The existence of the OII components at 300°C, in contrast to the other reports for 150°C [3,11], suggests the boundary of the OII phase region in the YBCO's structural phase diagram must be rectified at least up to 300°C. A roughly linear extrapolation of the phase fractions suggests that the pure OII phase at 300°C (200°C) corresponds to x ≈ 0.62 which is consistent with some other studies [11]. Although the OII phase is stoichiometric only for x = 0.5 in theory, it seems that the stability of the OII phase at elevated temperatures [200-300°C] demands more repulsive O-O forces by absorbing more oxygen atoms, 0.5<x<0.7.

Table 1

The Rietveld Refinement Method Results		χ^2	R_p	Tet.		Tet. Phase Frac.%	* O_{Tet}	OII			OII Phase Frac. %	** O_{OII}	Calculated Oxygen Content
				O_1	O_5			O_1	*** O_{1p}	O_5			
x~ 0.2	200˚C	3..32	0.092	0.05	0.0.5	85	0.085	0.55	0.32	0.05	15	0.145	x~ 0.23
	300˚C	2..99	0.091	0.085	0.085	92	0.156	0.48	0.21	0.017	8	0.058	x~ 0.214
x~ 0.3	200˚C	3.064	0.088	0.052	0.052	63.5	0.066	0.47	0.105	0.064	36.5	0.231	x~ 0.297
	300˚C	3.19	0.091	0.061	0.061	65	0.079	0.43	0.145	0.052	35	0.219	x~ 0.298
x~	300˚C	12.85	0.106	0.05	0.05	60	0.06	0.65	0.11	0.06	40	0.348	x~ 0.408

*The average of oxygen content in the basal plane for the Tet. phase

**The average of oxygen content in the basal plane for the OII phase

***The site occupancy for the counterpart of the O_1 site at the middle of the OII unit cell

The first column shows the oxygen content of the sample as expected during its preparation using the Sievert (volumetric) method and the last column shows the oxygen content obtained from the Rietveld refinement of the neutron diffraction data. The major discrepancy between them occurs for the low concentration case and this is probably due to tweed structure in the Tet. phase (low oxygen content). In the tweed structure oxygen atoms occupy the sites in the basal plane in an entirely random manner which makes proper modelling very difficult. The noteable points are:

i) With increasing oxygen content, the fraction of the ordered OII phase increases

ii) At each oxygen concentration, the OII phase fraction decreases at higher temperature (300°C).

References

[1]G. Ceder, M. Asta, W. C. Carter, M. Sluiter, M. E. Mann, M. Kraitchman, D. de Fontaine, *"Phys"*, .Rev.B 41 (1990) 8698.

[2] H. F. Poulsen, N. H. Andersen, J. V. Andersen, H. Bohr, G. O. Mouritsen, *"Phys"* , .Rev.Lett. 66 (1991) 465.

[3] H. F. Poulsen, M. von Zimmermann, J. R. Schneider, N. H. Andersen, P. Schleger, J. Madsen, R. Hadfield, H. Casalta, R. Liang, P. Dosanjh, W. Hardy, *"Phys."* , Rev.B 53 (1996) 15335.

[4] R. A. Young, *"The Rietveld refinement method"*, Oxford Univ. press (1993).

[5] J. D. Jorgensen, B. W. Veal, A. P. Paulikas, *"Phys."*, Rev.B 41 (1990) 1863.

[6] P. Schleger, R. A. Hadfield, H. Casalta H, N. H. Andersen, H. F. Poulsen, M. Von Zimmermann, J. R. Schneider, R. Liang, P. Dosanjh, W. N. Hardy, *"Phys."* , Rev.Lett. 74 (1995) 1446.

[7] R. Liang, D. A. Bonn, W. N. Hardy, *"Physica C"* , 236 (2000) 57.

[8] A. Algia, E. V. Anda, J. L. Moran-Lopez, *"Phys."* , Rev.B 42 (1990) 4288.

[9] A. G. Khachaturyan, J. W. Morris, *"Phys."* , Rev.Lett. 61 (1988) 215.

[10] W. Schwartz, O. Blaschko, G. Collin, F. Marucco, *"Phys."* , Rev.B 48 (1993) 6513.

[11] M. Zimmermann, J. R. Schneider, T. Frello, N. H. Andersen, J. Madsen, M. Kall, H. F. Poulsen, R. Liang, P. Dosanjh, W. N. Hardy, *"Phys."* , Rev.B 68 (2003) 104515.