In-situ HRPD study of superstructure OII phase in polycrystalline samples of YBCOx at 300 ºC

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Abstract: Superstructure orthorhombicII (OII) phase in polycrystalline samples of YBCOx was observed by using synchrotron in-situ high resolution powder diffraction (HRPD) techniques at 300˚C. Rietveld method (RM) refinement was employed to analyse the collected diffraction data under proper oxygen partial pressure atmospheres. Our study indicates that by oxygen uptake, the samples undergo structural phase transition from initial tetragonal phase to the superstructure OII phase with x ≈0.6. According to our previous study this transition follows 1st order Gibbs lever role. Evidence for exsistence of dominated OII superstructure in powder samples at 300 ˚C, makes a valuable correction on the YBCOx's structural phase diagram, which has been historically controversial and also would be interesting for applications.

Introduction

Oxygen deficient $YBa_2Cu_3O_{6+x}$ samples (YBCOx; 0<x<1) are the most applicable high temperature (HT_c) superconducting material and also important systems for basic studies in that field. Although, there is large number of studies on various features of the samples, very few in-situ experimental results have been reported on their structural phase transition procedure.

Theoretically, lattice-gas ASYNNNI models predict mainly three stable structural phases in moderate range of temperatures, < 400 ˚C, depending on oxygen stoichiometry of the samples: tetragonal (Tet), orthorhombic (OI) and superstructure orthorhombic2 (OII) [1,2]. Moreover, the OI(T_c:92K) and the OII(T_c:60K) phases are superconducting whereas, the Tet phase is semiconducting. In the Tet phase (x<0.2) short O-Cu-O chains form randomly in the basal plane along the *a* and *b* directions while, formation of long parallel chains just along the *b* direction is the main characteristic of the orthorhombic phases (for the OII superlattice phase, separation between the parallel chains becomes double) [1-6], Fig. 1.

To make samples with dominant OII phase at the moderate temperatures, isotherm techniques under proper oxygen partial pressures (PO_2) atmosphere can be employed [7,8]. As prepared samples, initially in the Tet phase (x≤0.3), via an isothermal oxygen uptake process undergoes a phase transition to the OII phase with x ≈ 0.5 (Tet/OII), by continuing the oxygen absorption process the OI phase becomes prevalent and OII/OI phase transition occurs finally. It should be pointed out that the nature of the phase transition processes (being first or second order) at moderate temperatures has been a controversial issue for long time [2,9-11]. In case of second order transition, it is quite clear that co-existence of the two phases (mixed phase region) is not expected at all.

In the literature observation of the superstructures was done mainly in single crystal samples at room temperature and the employed techniques are electron or neutron diffraction, x-ray diffuse scattering and recently electron and Raman spectroscopy [3-5, 12-14]. At moderate

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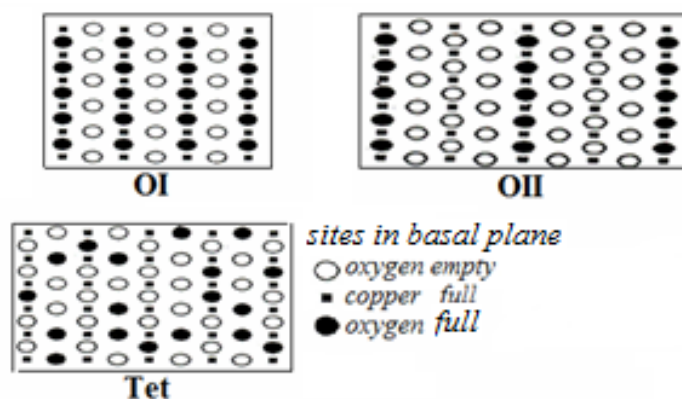
Fig 1 Schematic presentation of possible oxygen ordering in the basal plane and therefore, possible structural phases in YBCO$_x$ samples.

range of temperatures, scarcity of systematic studies is the result of difficulties in controlling of sluggish oxygen dynamic inside the sample. On the other hand, the ASYNNNI simulations are not certain about existence of the OII phase around 300˚C and spread range of the OII phase region always has been controversial.

According to our previous study [15], through the oxygen uptake process the OII phase fraction in the sample becomes increased, which is consistent with the well known Gibbs lever rule for first order Tet/OII phase transitions. Additionally, Seo et al. (2005) has also reported the co-existence of the Tet and OII phases in single crystal YBCOx sample at room temperature by using Raman spectroscopy technique [14].

Our motivation here is to employ synchrotron in-situ HRPD techniques to find out that if samples with dominated OII phase at 300 ℃ is available or not. In essence, while the samples are in thermodynamic equilibrium condition with their oxygen atmosphere, they are subjected to the diffraction measurements simultaneously. Furthermore, by considering the fact that empirical application of the single crystal samples is very limited, using polycrystalline powder samples is a noticeable feature of the present study.

Sample preparation and analysis method
The powder YBCO$_x$ samples were prepared by solid state method with high purity and particle size range of 1.5-5μm. Since diffusion dynamic of oxygen inside the samples at the moderate temperature is very slow and in order to optimise the in-situ measurement run times, a series of samples with different oxygen stoichiometries (0.4<x<0.7) were prepared via microbalance

gravimetric method (Intelligent Gravimetric Analyser; IGA Hiden Ltd.), following the isotherms reported by Schleger et al. [7] and Mercer et al. [8]. In doing so first, the samples became deoxygenated under vacuum (∼ 0.01 mbar) at 650 ˚C for about 2 hours, while their XRD patterns showed coincidence of [100] and [010] reflections (the Tet phase characteristic). Next, they were put inside the proper PO$_2$ atmosphere for several hours at the same temperature and relaxation of the samples after oxygen adsorption was examined by reproducibility of their XRD patterns.

In addition, for analysing the in-situ collected diffraction data, the full profile RM refinement (using GSAS package[1]) with Tet, OII, OI phase models has been employed. Table 1 shows the unit-cell atomic positions for the OII phase model.

In-situ synchrotron radiation diffraction at 300˚C
For conducting in-situ observation of the expected dominant OII phase in the powder samples, the high-resolution synchrotron radiation source (SRS) diffractometer (Darsbury, UK) was employed.
The diffraction measurements were done again under the proper PO$_2$ at 300˚C and the relaxation of the oxygen adsorbed samples before the final data collections were checked by, pattern's reproducibility of some quick run (10 minutes) pre-measurements (via monitoring of the diffractometer).

1-*GSAS* (**G**eneral **S**tructure **A**nalysis **S**ystem)
http://www.ccp14.ac.uk/solution/gsas/

Table 1

Atom type	x	y	z
Y	1/4	1/2	1/2
Y	3/4	1/2	1/2
Ba	1/4	1/2	0.185
Ba	3/4	1/2	0.185
Ba	1/4	1/2	0.825
Ba	3/4	1/2	0.825
Cu	0	0	0
Cu	1/2	0	0
Cu	0	0	0.355
Cu	1/2	0	0.355
Cu	0	0	0.645
Cu	1/2	0	0.645
O	0	1/2	0.355
O	1/2	1/2	0.355
O	1/4	0	0.355
O	3/4	0	0.355
O	0	0	0.185
O	1/2	0	0.185
O	0	1/2	0
O	0	1/2	0.645
O	1/2	1/2	0.645
O	1/4	0	0.645
O	3/4	0	0.645
O	0	0	0.815
O	1/2	0	0.815

In principal, the powder and polycrystalline samples are highly subjected to grain boundaries or other point and planer structural defects. To infer presence of the dominated OII phase from the diffraction data, different possible phase combination models (proposed in literature [16]) for the RM refinements were utilized and the best conformity between the diffraction data and the models was achieved when the OII model was employed solely. Details of the analysis (used models, conformity of the refinement, phase fraction, and lattice parameters) are shown in Fig.s 2 and in Table 2.

By examination of peak position marks (PPMs), under each of each patterns, in the Fig.2 (a,b,c) it is revealed that some weak reflections are distinctive characteristic of the OII phase (around $2\Theta \approx 32°$, 38°, 38° ... as the upper PPMs indicates). In principal, the super-lattice reflections are not supposed to be strong because of distractive effect between the superstructure and its regular structure in diffraction measurements.

Table 2 Results of the Full profile Rietveld refinements of the in-situ SRS diffractions according to different proposed models

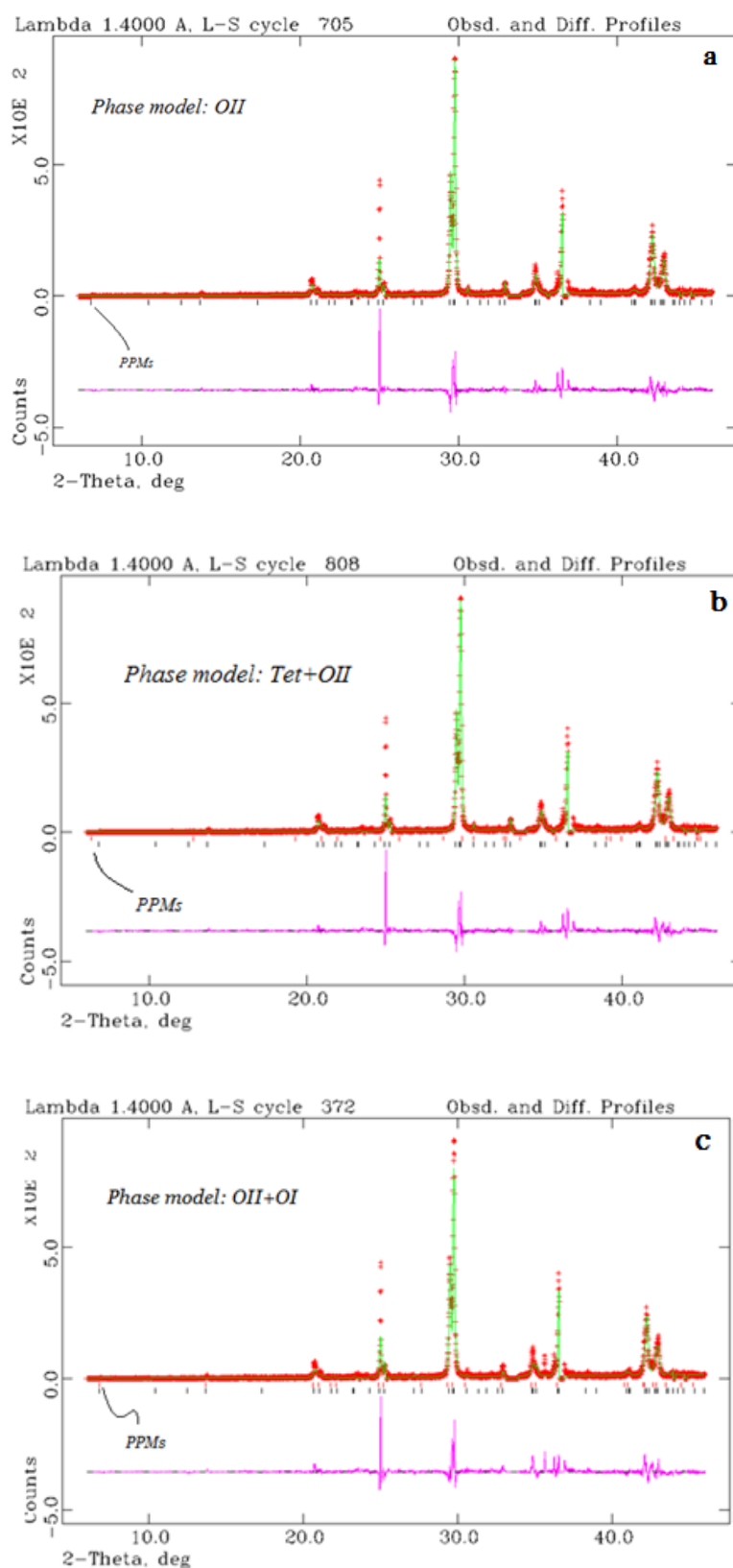| Proposed model	κ^2	L-S cycle number	Phase	a Å	b Å	c Å	Phase percent %
OII	1.704	753	OII	7.64	3.88	11.667	100
OI+OII	2.245	374	OI	3.826	3.88	11.667	49
			OII	7.64	3.896	11.7	51
OI+Tet	2.91	1615	OI	3.86	3.94	11.75	51
			Tet	3.9	------	11.81	49
OI	3.08	1344	OI	3.86	3.94	11.755	100
Tet+OII+OI	3.915	2903	Tet	3.836	------	12.477	24.2
			OII	7.68	3.9	12.3	51
			OI	3.78	3.95	13.46	24.8
Tet+OII	1.74	869	Tet	3.85	------	13.05	5
			OII	7.64	3.88	11.68	95

Fig 2 The in-situ SRS diffraction refined patterns by using a-only OII phase, b-mixed Tet+OII phases and c- mixed OII+OI phases model in the refinement procedure. PPMs belong to the OII phase are shown by the lower row in the figures b and c. Details of the refinement output are shown in table 2.

In the table the conformity of the refinements are indicated by κ^2 parameter and shows least square fitting value between the built diffraction model and the collected diffraction data; therefore, the lower κ^2 values show more reliability of the selected model in the RM analysis. To the best of our knowledge, the added phase makes more parameters available for the refinement procedure, therefore; the least square fitting process could be facilitated. On the other hand, as the table shows when we added extra phase model to the OII phase the refinement's κ^2 value increased unexpectedly so it is an indication for real conformity between the OII model and the diffraction data.

By the way, the L-S number on the top of each refined pattern in Fig. 2 shows number of the performed least square fitting cycles in the RM analysis. Its largeness implies that how much difficult and time-consuming has been the refinement procedure and unreasonable large number of the cycles (>1000) could be interpreted as an artificial effort so it is not justified, obviously [17].

Unfortunately, some unknown intensive reflections originated from the metallic sample holder inside the furnace were strongly attached to the sample's genuine reflections (such as the peak around 25˚) and they were the most important negative factors in the refinements.

Finally, by using microbalance gravimetric technique in the samples preparation step and also from RM analysis of the in-situ HRPD data (with different trial phase models) we were convinced that the single phase of the OII superstructure has been dominant in the powder sample with x≈0.6 at 300˚C.

Conclusions

By using microbalance gravimetric technique (IGA apparatus) for preparing the powder samples and under highly-controlled oxygen partial pressure in-situ SRS high resolution diffraction measurements, a dominated OII single phase in the samples was observed around x≈0.6 at 300 C.

This result along with our previous paper [15], show a systematic study of the structural phase transition for the YBCO$_x$ powder samples from tetragonal to superstructure OII phases. Full profile Rietveld refinement method of the diffraction data indicates that the transition to the OII phase occurs via a mixed phase region in agreement with the 1st order Gibbs lever rule, although the ASYNNNI simulations are not certain.

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