Determination of structural changes of $YBa_2Cu_3O_{6.94}$ by X-Ray diffraction

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Abstract

X-ray diffraction (XRD) patterns of the samples $YBa_2Cu_3O_{6.94}$ after slow heating from 300 K to 530 K (less than 1 K/hour) and annealing at 530 K during one month demonstrate the decreasing of intensity of diffraction peaks and its broadening. Peak broadening is often assumed to results from coherent scattering domain sizes, its distribution, strain and disorder. Modeling of all possible contributions to XRD profiles were carried out. Usefulness of such approach for correlation of superconducting properties to actual structure is discussed.

Key words: X-ray diffraction, superconductivity, annealing at 530 K, YBCO-system

1. Introduction

On the temperature dependence of resistivity $\rho(T)$ of the optimum doped (T_c=92 K) HTSC $YBa_2Cu_3O_{6.94}$ the maximum of $\rho(T)$ in the vicinity of $T_{max} \sim 560$ K is found out similary to Bi-based HTSC [1]. At usual heating rate and cooling (~ 1 K/min) the typical metal dependence $\rho(T) \sim T$ without any anomalies is observed. At slow heating ($\sim$ 1 K/hour) $\rho(T)$ sharply grows and culminates at $\sim$ 560 K. Increase of $\rho(T)$ is about 75% from the resistivity observed at fast heating, and it is not connected with changing of the oxygen contents in a sample. What are the structural modifications lead to change of concentration of carriers of a current in a conduction band which caused so strong increase of resistivity? It is the most natural to connect this anomaly with redistribution of oxygen in a mobile sublattice similarly to Bi-based HTSC [1]. The structural phase diagram for Y-123 is reliably enough established at present time [2]. But at the oxygen content $x > 6.82$ and $T < T_{orto-tetra}$ the phase O-I is realized only. A series of structural changes of 123 phases connected to deformation of CuO_2 plane take place in area of a O-I. A non-uniform character of samples - mixed of optimum doped and over doping conditions is marked on the spectroscopic data at the phase transition through a point optimum doped (x=6.95). So that to understand, what real structural changes occur at the slow heating in a range of temperatures from room up to 560 K, are necessary additional diffraction researches.

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2. Results and discussion

2.1. *Sample preparation and characterisation*

The starting material was ceramic $YBa_2Cu_3O_{6.94}$ prepared by standard sinter-processing procedure. The oxygen content was determined by an iodometric method [4]. The resistivity was measured by the standard four-probe method at 77-1100 K. Weight technique was used for checking of oxygen content changes

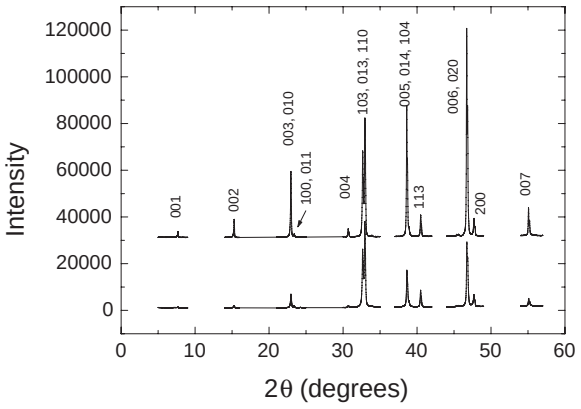

Fig. 1. X-Ray patten of investigation samples: top curve - for initial sample; bottom curve - for sample after slow heating up to 560 K.

during the temperature dependence measurements. Diffraction patterns of samples were recorded on a Philips PW 1050 diffractometer using $CuK\alpha$ radiation. Whole XRD patterns intensities were measured for 100 s with 0.1 degree steps. Individual reflections intensities were measured for 60 s per 0.01 degree steps.

2.2. *X-ray diffraction*

X-ray diffraction patterns obtained from the slow heated sample indicate that structural changes affect the *c*-axis stacking sequence in studying sample (modulation of the *c*-axis interferences). General view of both spectrum (Fig.1) is very similar. The both samples is mono phase. The parameters of unit cell (determined on diagnostic reflexes 006, 020, 200) of the sample after heating practically have not changed ($a = 3.813\mathring{A}$, $b = 3.879\mathring{A}$, $c = 11.665\mathring{A}$). The both samples have the orthorhombic structure with $(b-a)/(b+a) = 0.0086$. According to experimental dependence of parameter from oxygen concentration [3] the oxygen contents in a sample corresponds to x=6.92-6.93, i.e. the X-ray data confirm, that the sample after heating has remained in optimum doped states. However more detailed investigation has shown, that during slow heating a sample up to 560K some structural changes take place which result in some features on diffraction patten. The peak corresponding to 001 basal reflection of $YBa_2Cu_3O_{6+x}$ reveals shape asymmetrical distortions and, besides, a broad unknown peak is appeared (Fig. 1).

2.3. *Structural modeling*

The appearance of additional peaks on diffraction pattern indicate that temperature treatment affects the c-axis stacking sequence in studying sample (modulation of the c-axis interferences). For interpretation of diffraction spectra changes full profile analysis consisted in comparison of experimental and theoretical X-ray curves calculated for different structural models of layer stacking has been employed. The calculation performed by means computer program developed by A.S.Bookin [5] takes into account the possibility of coexistence of different kinds of layers in stacking and different types of their alternation. For construction of the structural models we use the results of the structural refinements of $YBa_2Cu_3O_{6+x}$ phases. A number of possible structural models describing chemical inhomogeneities and different variants of stacking faults were seen. One of the possible model for interpretation of the additional peak near 001 basal reflection may be the formation of a stacking fault which associated with insertion of an extra CuO-chains between Ba atoms and shift by one-half lattice parameter along the *b*-axis and one-sixth the lattice parameter along the *c*-axis (Fig. 1). It is necessarily to notice, that the process of modelling is quite enough complicated, and receiving results only first step to this problem investigating.

3. Conclusion

In summary, the calculations of X-ray patterns were carried out on the base of matrix method taken into account the possibility of coexistence of different kinds of layer in stacking. The modelling has been provided for profiles of 00l reflections is an effective approach to characterize structural ordering - disordering of HTSC materials.

Acknowledgements

The work was partially supported by Russian Foundation of Basic Research (Grants No: 00-02-17914; 00-15-97448), and Government Scientific Program of Condensed Matter Physics (Grant No 98009, Section "Superconductivity").

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