YBa$_2$Cu$_3$O$_{7-x}$ 240 K Phase Transition

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YBa$_2$Cu$_3$O$_{7-x}$, ceramic samples have been investigated simultaneously by the thermal expansion and the acoustic emission methods during thermocycling through 200–300 K into liquid nitrogen steam. No jumps in the dilatation curves but change in the slope of one has been found at 228 and 234 K on heating and cooling respectively. These points are accompanied by the acoustic emission signals, a small value testifying for oxygen atoms displacement into the crystal lattice. On the basis of these measured experimental data, a thermal expansion coefficient $\alpha$ and a specific capacity $c_m$ have been calculated. By this $c_m$ value an oxygen atom activation energy $E_A = 0.15$ eV has been calculated. It is shown that an isostructural oxygen-displacement second-order phase transition takes place between certain orthorhombic phases in YBa$_2$Cu$_3$O$_{7-x}$ near 240 K.

KEY WORDS: thermal expansion; acoustic emission; activation energy; phase transition.

1. INTRODUCTION

In the last few years, YBa$_2$Cu$_3$O$_{7-x}$ 240 K phase transition (PT) has been intensively investigated by different methods. By roengenometry the jumps of lattice’s parameters were observed without changing the symmetry of one [1]. By internal friction 7 K temperature hysteresis was measured in the region of 237 and 244 K respectively [2]. By the mechanics study Young modulus hysteresis was shown near 250 K [3]. By the anelastic relaxation an abrupt change of internal friction and frequency was obtained at 235 K [4]. The results of direct dilatometric measurements are in rather poor agreement with one another. In [5] the thermal expansion coefficient $\alpha$ had a sharp maximum at 240 K during heating but not during cooling. In [6] the smeared minimum of $\alpha$ occurred at 220 K, and in [7] there were no dilatometric anomalies in a reviewed region.

There is no consensus on this PT mechanism too. Based on Young modulus variation and abrupt changes of internal friction and frequency, a diffusion or martensitic PT would take place [4]. On the other hand, the lattice symmetry constancy of this PT is obviously to be an isostructural PT. In this case an isostructural PT would occur because of replacements of the oxygen atoms in the basis plane of a crystallographic lattice.

Indeed, the theoretical calculation of $T-x$ diagram was performed to show the oxygen atoms displacement along CuI–O4 chains near 240 K [8]. These oxygen replacements were discussed as first- or second-order PT between certain local orthorhombic phases with a stoichiometry different than that of the neighboring unit cells or domains in YBa$_2$Cu$_3$O$_{7-x}$ ($x < 0, 1$) material. However, the displacement activation energy of these oxygen atoms was not calculated or measured. Meanwhile, we cannot reach correct conclusions [8] without knowing the oxygen activation energy near the 240 K region. Oxygen atoms displacements in a crystallographic lattice, as a rule, induce dilatometric anomalies and would simply be detected by an acoustic emission method, as was shown earlier in [9–11].

To investigate the YBa$_2$Cu$_3$O$_{7-x}$ 240 K region and calculate the oxygen atoms activation energy we simultaneously applied the thermal expansion and the acoustic emission methods. By the thermal expansion curve behavior and the acoustic emission activity we will discuss this PT type and by the thermal
expansion coefficient we will estimate the activation energy value of oxygen atoms.

2. EXPERIMENTAL

YBa2Cu3O7–x ceramic samples, with Tc = 92 K, ΔT = 2 K, and ρ = 4.5/5.0 g · cm⁻³, were investigated by the origin technique [12]. In a cryogenic chamber a sample was put on the polished surface end of a quartz glass cylindrical waveguide, which was entered into the chamber from below. A ceramic PZT-19 piezoelectric sensor was pasted to the cold opposite surface end of the waveguide. Two rods of a differential dilatometer were entered into the chamber from above. The error of a differential dilatometer was not more than 10⁻⁷. The temperature was measured by a thermocouple, whose junction was in contact with the sample.

A liquid nitrogen steam was being blown through the chamber with regulated speed. The related thermal expansion ΛL/L and the acoustic emission (AE) activity N were simultaneously measured during the samples’ thermocycling through the 200–300 K temperature region with a speed of about 1 K/min.

3. RESULTS AND DISCUSSION

Results of YBa2Cu3O7–x ceramic samples measured near 240 K are shown in Fig. 1. The dilatation curves are monotonic, without discontinuities and jumps, but vary their slope on the common angle: at 238 K on heating and at 228 K on cooling. The temperature hysteresis is just 6 K, similar to that reported in [2]. The contraction points are accompanied by AE signals. These results are reproduced through thermocycling. From these curves the thermal expansion coefficient α is determined and the molar specific capacity cₘ is calculated by Grunizen formula:

$$c_\text{m} = \frac{3V_\text{m}}{\gamma X}$$

where $V_\text{m} = 11 \times 10^{-6}$ m³ · mole⁻¹, $X = 6 \times 10^{-12}$ m² · N⁻¹, and $\gamma = 3.4$ [7].

The results of calculation are shown in Fig. 2. α exhibits terminal jump and its (T) dependence makes the rectangular loop. The absence of sample’s volume dilatation jumps and α hysteresis loop are characterized for PT of second order. Detected AE signals additionally confirm the suggestion that oxygen atoms replacements take place in the crystallographic lattice. Perhaps, replacing oxygen atoms induce some moving of the domains walls, which radiate acoustic waves [3,10].

Let us estimate an activation energy of these oxygen atoms replacements as:

$$\Delta E = \frac{T_s \Delta C_m}{V_\text{i}} \cdot 10^{19}$$

where $V_\text{i} = 170$ Å³, unit cell volume at 250 K.

From Eq. (2) ΔE = 0.15 eV. This activation energy found near 240 K agrees satisfactorily with the one needed for oxygen atoms’ jumps on Cu–O plane near the superconducting PT [2].

Thus, the coincidence of activation energies of these two oxygen atoms in nearest temperature regions confirms the conclusions [8] about the existence of some stable phases with different oxygen content in YBa2Cu3O7–x. As followed from [8], at low temperatures these phases are orthorhombic and