Crystal structure of Hg,Tl-1223 HTSC compound under high pressure and low temperature

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Abstract. Powder diffraction data for high temperature superconducting compound Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+δ} at pressure range 0-20 GPa and temperature interval 100-300 K are presented. Unit cell parameters and atomic coordinates are calculated. It is found, that Ba-atoms do not shift towards HgO_2-planes and splitting of BaO-planes do not decrease with external pressure. This result contradicts with evident charge transfer between HgO_x- and CuO_2-planes. State of buckling of CuO_2 planes changes with pressure from slightly positive (for (zO_2-zCu)value) at ambient pressure to strongly negative at P \geq 1.56 GPa. A growth of superconducting transition temperature as a function of the external pressure even for overdoped Hg,Tl-compounds up to P \approx 15 GPa we explain as a result of an interplay between a sequence of pressure induced charge transfer and observed change of crystal structure.

1. Introduction
It is well established that superconducting transition temperature for HTSC compounds has a parabolic shape as a function of doping state. Moreover it seems to be established that external pressure leads to an increase of doping state for HTSC compounds, and for underdoped materials at first leads to a growth of T_c and, at higher pressure, to its decay. However, T_c value for mercury-based HTSC compounds drastically increases as a function of external pressure even for overdoped samples [1, 2, 3]. The reason of this behavior is still under investigation. It is assumed that growth of T_c value is caused by so called an "intrinsic term" [2, 3] (for example, CuO_2 planes become more flat or the thickness of the "metallic" layer into the unit cell diminishes in comparison with "superconducting" layer [3]). This "intrinsic" term may lead to an opposite effect than the charge transfer between HgO_x-planes and superconducting CuO_2-planes. To study the origin of this possible "intrinsic" structural effect we have performed the study of the crystal structure for Hg,Tl-1223 slightly overdoped compound applying an external pressure up to 20 GPa in the temperature range 100-300 K.

2. Experiment
Samples with T_c \approx 127 K were synthesized by Prof. I. Bryntze, Stockholm University, Arrhenius Laboratory [4]. Powder diffraction experiments were performed at SPring-8 synchrotron source,
BL10XU beamline using diamond anvil cell (DAC) and helium cryostat. The Imaging Plate R-AXIS IV was used as a detector, the resolution was 0.10 mm, the size of a sensitive area 300×300 mm, monochromatic wavelength $\lambda = 0.4959 \text{Å}$. The experiment was performed under the projects 2002A0629-ND2-np and 2004B0763-ND1a-np. Experiment at ambient pressure was performed earlier using STOE diffractometer [5]. Crystal structure refinement was carried out using full profile analysis with GSAS program [6]. The following starting model was used: Ca (0.5, 0.5, 0.3970), Hg and Tl (0, 0, 0), Ba (0.5, 0.5, 0.1760), Cu1 (0, 0, 0.5), Cu2 (0, 0, 0.3020), O1 (0, 0.5, 0.5), O2 (0, 0.5, 0.3040), O3 (0, 0, 0.1320), O4 (0.5, 0.5, 0), the unit cell is shown in Figure 1. The following discrepancy factors were achieved: $R_B \equiv \frac{\sum |F_c - F_o|}{\sum I_o} \approx 17 - 22\%$, $R_p \equiv \frac{\sum |I_c - I_o|}{\sum I_o} \approx 6.7 - 7.9\%$, $\omega R_p \equiv \sqrt{\sum \omega (I_o - I_c)^2 / \sum \omega I_o} \approx 9.05 - 10.8\%$ for various temperature and pressure values, where $F_o$ and $F_c$ are the observed and calculated structure factors, $I_o$ and $I_c$ are the observed and calculated intensities, $\omega$ is statistical weight. Discrepancy factors are relatively high because of presence of the impurities (complex barium cuprates, $\approx 5\%$) and the diffraction lines arising from DAC.

**Figure 1.** The unit cell of Hg$_{0.8}$Tl$_{0.2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$. Hg and Tl atoms are shown by blue symbols, Ba - yellow, Ca - green, Cu-O structural units are shown as red fragments. Half of the $dn$ distance is shown as the arrow.

3. Results and discussion

Calculated unit cell parameters in $c$-direction as a function of temperature for different values of external pressure are presented in the Figure 2.

Splitting of CuO$_2$-layers calculated as $c \times (zO2-zCu)$ is presented in the Figure 3. This splitting decreases as a function of an external pressure; at almost ambient pressure CuO$_2$-layers are practically flat; when pressure rises up to 1 GPa the splitting becomes negative and large by the absolute value. The change of the sign of $(zO2-zCu)$ value may be caused by high charge carrier concentration in the CuO$_2$-layers. At the same time, splitting of the BaO-layer, calculated as $c \times (zBa-zO3)$ does not decrease (Figure 4) but, in contrary, increases with pressure.
Figure 2. Unit cell parameter $c$ as a function of temperature for Hg,Tl-1223; 1 - ambient pressure, 2 - 0.35 GPa, 3 - 1 GPa, 4 - 1.56 GPa, 5 - 20 GPa.

Figure 3. Splitting for CuO$_2$-planes calculated as $c \times (z_{O2} - z_{Cu})$ as a function of temperature for Hg,Tl-1223; the notation for different pressure is the same as for Figure 2.

It is commonly accepted that splitting of BaO-layer is linearly proportional to the difference in Coulomb charge between so called ”charge reservoir” HgO$_x$-layer and superconducting CuO$_2$-layer [7]. From the data shown in Figure 4 we do not see the charge transfer between HgO$_x$ and CuO$_2$ planes in studied pressure range.

Figure 4. Splitting for BaO-planes calculated as $c \times (z_{Ba} - z_{O3})$ as a function of temperature for Hg,Tl-1223; the notation for different pressure values is the same as for Figure 2.

Figure 5. Thickness for the ”metallic layer” $dn$ as a function of temperature for Hg,Tl-1223; the notation for different pressure values is the same as for Figure 2.

As it was reported earlier [2], growth of $T_c$ in the mercury-based HTSC compounds under an external pressure may be a sequence of decrease of the thickness of the ”metallic layer” $dn$ (distance between CuO$_2$ fragments separated by HgO$_x$-layers, Figure 1). Calculated values of $dn$ are shown in Figure 5. The metallic layer thickness $dn$ slightly increases for $P=0$-1.5 GPa and rapidly decreases when the pressure becomes as high as 20 GPa, a growth of $dn$ occurs exactly in the pressure range when the state of buckling of CuO$_2$ layers remains small (Figure 3).

Thus, there are two different pressure intervals: 1) $P \leq 1.5$ GPa, when CuO$_2$ splitting remains small and ”metallic layer” thickness $dn$ increases; and 2) $P \geq 1.5$ GPa, when $dn$ drastically
diminishes and splitting of CuO$_2$-layer becomes large by absolute value and negative. From literature data [1, 2, 3, 8] $T_c$ starts to decrease for $P \geq 15$ GPa for overdoped materials. The change of a sign for the value of splitting for CuO$_2$-layer at high pressure may be explained as a result of high charge carrier concentration in CuO$_2$-plane due to interlayer charge transfer. However, we do not see a corresponding decrease of Ba-O layer splitting (Figure 4). We suppose, that observed crystal structure features (mainly a growth of metallic layer thickness $dn$) lead to a compensation of the increase of the doping state at low pressure regime and, as a consequence, to an increase of the critical temperature $T_c$ with pressure.

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