SYNTHESIS AND PROPERTIES OF SUBSTITUTED
Hg-BASED SUPERCONDUCTORS

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2004
«... – Ну вот, например, вы, ученые. Надеетесь вы получить... что-нибудь фундаментальное, что-нибудь такое, что действительно способно перевернуть науку, технологию, образ жизни?.. – ... Когда речь идет о таких серьезных вещах, я предпочитаю осторожный скепсис. Если исходить из того, что мы уже получили, впереди целый спектр возможностей, и ничего определенного сказать нельзя...»

А. и Б. Стругацкие. “Пикник на обочине”

«... – Well, look at you, for instance, you’re a scientist. Are you hoping for something fundamental... something that will alter science, technology, our way of life?.. – ... When the subject is something serious, I prefer to revert to healthy careful scepticism. Based on what we’ve already received, a whole range of possibilities is raised, and I can say nothing specific about it...»

A. & B. Strugatsky “Roadside picnic”

Translated from Russian by Antonina W. Bouis
This thesis is focused on studies of substituted Hg-based superconducting copper oxides \((\text{Hg}_{1-x}\text{M}_x)\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta})\). These compounds are promising objects of investigation, not only from a fundamental point of view but also because of their high values of superconducting transition temperature \((T_c)\) and irreversibility field \((H_{irr})\).

The first part of the thesis is devoted to optimization of the synthesis procedure for Hg-based cuprates. The influence of different parameters \((T, t, p(\text{Hg}), p(\text{O}_2))\) on the synthesis of these compounds in sealed silica tubes was studied. Optimal conditions yielded samples containing up to 95\% of \(\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\) (Hg-1223). The formation of solid solutions with the formula \((\text{Hg}_{1-x}\text{Cu}_x)\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}\) (where \(x \leq 0.5\)) was also established. Another technique was developed, using LiF as a flux, for synthesis of samples containing up to 90\% of the \(\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}\) (Hg-1212) phase.

The second part concerns synthesis and studies of oxyfluorides using Hg-1212 and Hg-1223 as starting materials together with \(\text{XeF}_2\) as a fluorinating agent. It was found that oxyfluorides of both phases have a parabolic dependence of \(T_c\) vs. \(a\) parameter as well as enhanced \(T_c\) values \((\Delta T \approx 3–4\,\text{K})\) in comparison with optimally doped non-fluorinated analogues. The crystal structure of Hg-1223 oxyfluoride was studied by X-ray powder and neutron diffraction methods. It is suggested that chemical modification of the crystal structure leads to a decrease in Cu–O distance without noticeable change in Cu–O–Cu angle (in the (CuO\(_2\)) layers), which may be the significant factors influencing this \(T_c\) increase. Hg-1223 oxyfluoride was also studied under high pressure for first time. It was found that this compound has a record-high \(T_c\) value \((\approx 166\,\text{K})\) at \(P \approx 23\,\text{GPa}\).

The last part describes the investigation of substituted Hg-based superconductors in the series \((\text{Hg}_{0.9}\text{M}_{0.1})\text{Ba}_2\text{CuO}_{4+\delta}\) \{(Hg,\text{M})-1201\}, where \(\text{M} = \text{Tl}, \text{Pb}, \text{W}, \text{Mo}, \text{Nb}\) and \(\text{V}\). A comprehensive study of these compounds by various methods (X-ray powder diffraction, EDX, IR-, EXAFS- and XANES -spectroscopy) indicated that the change of charge carrier doping level is a crucial factor determining the irreversibility line. \((\text{Hg}_{0.9}\text{Mo}_{0.1})\text{Ba}_2\text{CuO}_{4+\delta}\) showed the most improved irreversibility line position among the (Hg,\text{M})-1201 compounds studied in this series.
The work on this thesis was mainly carried out during a period of 5 years, September 1999 – September 2004, at the Inorganic Chemistry Department, Arrhenius Laboratory, Stockholm University (Sweden) and Inorganic Crystal Chemistry Laboratory, Inorganic Chemistry Division, Department of Chemistry, Moscow State University (Russia), in collaboration with the Free University of Berlin (Germany) and the Synchrotron Radiation Research Center (NSRRC) (Taiwan). Some parts of this work were also performed at C.R.T.B.T., C.N.R.S. (France), Moscow State Academy of Fine Chemical Technology (Russia) and Institute of Organoelement Compounds, Russian Academy of Sciences (Russia).

The thesis is organized as follows.

The introductory part contains a brief overview of the crystal chemistry of Hg-based superconducting cuprates and their substituted analogues. It also describes various problems related to the synthesis of these compounds. The last chapter of this part is devoted to a short description of the relationship between the crucial superconducting parameters (\(T_c\) and \(H_{irr}\)) and various structural factors.

The experimental part comprises a detailed description of the synthesis techniques used and also contains some information about the investigation methods applied.

The last part of the thesis presents a discussion of the principal results obtained, followed by conclusions and list of references.
This thesis is mainly based on the following publications:


Publications not included in the thesis:


Publications outside the scope of the thesis:

X. K.A. Lokshin, **D.A. Pavlov**, M.L. Kovba, E.V. Antipov, I.G. Kuzemskaya, L.F. Kulikova, V.V. Davydov, I.V. Morozov, E.S. Itskevich. “Synthesis and characterization of overdoped Hg-1234 and Hg-1245 phases; the Universal behavior of $T_c$ variation in the HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ series”. *Physica C* (1998), 300, 71–76.


XIII. R. Stern, I. Heinmaa, **D.A. Pavlov**, I. Bryntse. “Exploring the oxygen order in Hg-1223 and Hg-1201 by $^{199}$Hg MAS NMR”. In manuscript (2004).
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ABBREVIATIONS AND SYMBOLS

All the new terms essential for further text are **highlighted** at the first appearance, which is usually followed by their definition. The most common abbreviations and symbols in this thesis are summarized below. The references available in the text on detailed explanation of several symbols are given in brackets (e.g. I.2.3):

I. Symbols and abbreviations denoted some structural parameters:

The abbreviation system, which was often used instead of “large” chemical formulas of studied compounds, is clearly described in the text (I.2.3). In short, formulae of the main studied compounds are denoted as:

- **Hg-1201**: \( \text{HgBa}_2\text{CuO}_{4+\delta} \);
- **Hg-1212**: \( \text{HgBa}_2\text{Ca}_{2}\text{Cu}_2\text{O}_{6+\delta} \);
- **Hg-1223**: \( \text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta} \);

\((\text{Hg,M})-12##\): \( \text{(Hg}_{1-x}\text{M}_x\text{)}\text{Ba}_{2-n}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \), where:

- \( x \): substitution extent of \( \text{M}^{z+} \) for \( \text{Hg}^{2+} \) cation;
- \( n \): number of \( \text{CuO}_2 \) planes or ordinal number of the homologues series member (I.2.1);

Other symbols denoted some structural parameters are the following:

- \( a, c \): tetragonal lattice parameters of Hg-based cuprates;
- \( c/a \): also referred to structural anisotropy;
- \( \_\_ \): vacancy;
- \( \angle \): angle, for instance, \( \angle \text{O–Cu–O} \): the O–Cu–O angle;
- \( d \): distance, for instance, \( d_{\text{Cu–O}} \): the Cu–O distance;
- \( \text{CN} \): coordination number;
- \( \text{eq}, \text{ap} \): equatorial (or in-plane) and apical (out-of-plane) positions, respectively;
- \( \delta \): extra-oxygen content (concentration) (I.2.2, I.2.4);
- \( \delta_{\text{opt}} \): optimal value of \( \delta \) (I.2.4);
- \( p \): number (concentration) of charge carriers, *i.e.* holes (I.2.5);
- \( v_{\text{Cu}}, v_{\text{av Cu}} \): copper oxidation state, average copper oxidation state (I.2.2, I.2.4).

II. Symbols representing some synthesis parameters:

The main symbols related to some synthesis parameters are the following:

- \( T \): temperature of annealing;
- \( t \): synthesis duration;
- \( p(\text{O}_2) \): partial oxygen pressure inside the tube;
\( p(\text{Hg}) \): partial mercury pressure inside the tube;

\( m_{\text{HgO}, \text{ex}} \): excess amount of mercury oxide (II.1.2);

\( l, \varnothing \): length and diameter of tubes, used for the synthesis;

\( P \): applied pressure in a high-pressure synthesis technique.

III. Symbols of various magnetic characteristics etc.:

The most common symbols of some magnetic (also superconducting) parameters are the following:

- \( T_{\text{c}} \): transition temperature into superconducting state (a subscript “c” means critical);
- \( T_{\text{c}, \text{max}} \): the optimal value of \( T_c \) reachable for any particular cuprate (I.2.4);
- \( T_{\text{onset}}, T_{\text{mid}} \): the onset and the midpoint \( T_c \)-values, respectively (III.2.2);
- \( H, H_{\text{c1}}, H_{\text{c2}} \): values of magnetic field, the first and second critical fields, respectively; (I.5.1);
- \( H_{\text{irr}} \): the value of irreversibility field (I.5.1);
- \( IL \): irreversibility line (I.5.1);
- \( M, \Delta M \): magnetization and width of magnetization hysteretic loop, respectively;
- \( \chi \): magnetic susceptibility;
- \( \text{ZFC, FC} \): zero field cooled and field cooled measurements of superconductors, respectively;
- \( \text{NS} \): non-superconducting sample.

IV. Abbreviations of investigation methods often mentioned in the text:

- \( \text{XRD} \): X-ray diffraction analysis;
- \( \text{ND} \): neutron diffraction analysis;
- \( \text{EDX} \): energy dispersive X-ray spectrometry;
- \( \text{SEM} \): scanning electron microscopy (also scanning electron microscope);
- \( \text{TEM} \): transmission electron microscopy;
- \( \text{IR} \): infrared spectroscopy;
- \( \text{EXAFS} \): extended X-ray absorption fine structure spectroscopy;
- \( \text{XANES} \): X-ray absorption near edge structure spectroscopy;
- \( \text{IT} \): iodometric titration.
I. Introductory part

CHAPTER 1. INTRODUCTION

It is well known that Hg-based superconducting cuprates (HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$) show the highest transition temperatures into the superconducting state ($T_c$), both at normal pressure (for instance, HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ has $T_c = 135$ K) and high pressure (for HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ $T_c \approx 164$ K at $P = 31$ GPa). That is why these compounds are promising candidates for a number of possible applications. However, the scope of Hg-based superconductors application is not all wide, because of difficulties in reproducible synthesis of samples containing only one superconducting phase, the toxicity of several substances that may be formed during the synthesis (especially metallic mercury), chemical instability of the cuprates obtained, low values of irreversibility fields ($H_{irr}$) etc.

Nevertheless, it has been recently shown that synthesis of substituted Hg-based cuprates may overcome many of the problems listed above. Substitutions result both in structural distortions and changes of the doping level, which yields compounds with changed (preferably enhanced) superconducting characteristics (i.e. $T_c$ or $H_{irr}$). It should be noted that the relationship between different structural factors and $T_c$ values has been investigated rather comprehensively, whereas their correlations with $H_{irr}$ has not been studied nearly as thoroughly up to now. There are several hypotheses in the literature, attempting to explain the increase of $H_{irr}$ for substituted compounds.

Therefore, synthesis of substituted compounds using of various methods, optimization of synthesis procedures and, finally, investigation of the influence of these substitutions on $H_{irr}$ enhancement are crucial and topical problems, and they are thus the main goals of this work.
CHAPTER 2.
GENERAL ASPECTS OF THE CRYSTAL CHEMISTRY OF Hg-BASED CUPRATES

I.2.1. Layers and slabs, homologous series

Hg-based complex copper oxides (or cuprates), as well as all other high-$T_c$ cuprates, have layered crystal structures (see Figures 1–3). There exist four different types of layers. First of all, there are (CuO$_2$) layers, varying in number from 1 to $n$ per unit cell. These (CuO$_2$) layers may be separated from each by (Ca ) layers; evidently (n–1) such layers per unit cell in general. According to current physical theory, the (CuO$_2$) layers are responsible for the superconductivity of these compounds. Thus, $n$ (CuO$_2$) and (n–1) (Ca ) layers together form a so-called conducting block, which has a perovskite-type crystal structure (Figure 1b).

![Diagram](image)

Figure 1. Scheme representing an intergrowth (c) between rock salt-type (AX) (a) and perovskite-type slab (ABX$_3$) (b).

Between the conducting blocks there are insulating slabs. These slabs in Hg-based cuprates consist of insulating (HgO$_3$) and (BaO) layers with a stacking sequence that results in a rock salt-type crystal structure of the insulating slab (Figure 1a).

---

1 Investigation of different layered cuprates has up to now revealed the existence of phases with $n_{\text{max}} = 9$. 
Thus, the layer stacking sequence along the $c$ axis in the Hg-based cuprates could be represented schematically as follows (Equation 1, Figure 2):

\[
\text{— } [\text{(BaO)}(\text{HgO}_6)(\text{BaO})]((\text{CuO}_2)((\text{Ca }))(\text{CuO}_2)_{(n-1)})\text{—} \quad (1)
\]

It is clear that, according to this formula, there exist several compounds that differ from each other only in the number of $(\text{CuO}_2)$ and $(\text{Ca }$) layers per unit cell. One may say that these similar compounds form a \textit{homologous series}, where each compound can be denoted as \textit{homologue $n$} or \textit{$n^{th}$ member} of the series.

\textit{Figure 2.} Stacking sequence of layers along $c$ axis for the crystal structure of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2+2n+\delta}$ ($n = 2$) cuprate phase.

It is clear that, according to this formula, there exist several compounds that differ from each other only in the number of $(\text{CuO}_2)$ and $(\text{Ca }$) layers per unit cell. One may say that these similar compounds form a \textit{homologous series}, where each compound can be denoted as \textit{homologue $n$} or \textit{$n^{th}$ member} of the series.
I.2.2. Stability criteria

In order to yield a stable compound, the stacking sequence presented above, should obey geometrical and charge criteria of stability.

The geometrical criterion can be described as a number of stacking sequence rules. According to this criterion the structure is stable if the cation–oxygen distances in any one layer are commensurate with analogous distances in layers above- and below. This commensurability is especially important between conducting (CuO₂) layers and adjacent (BaO) layers, because severe distortions of (CuO₂) layers usually result in lower $T_c$ (and also deterioration of some other superconducting characteristics).

The commensurability between (BaO) layers and (HgO$_{\delta}$) layers is less important, because Hg$^{2+}$ cations have a linear (“dumbbell”) coordination (CN = 2) with apical oxygen atoms ($d_{\text{Hg-O}_{\text{ap}}}$ ≈ 2.0 Å), while the Hg–O$_{\text{eq}}$ distance in the (HgO$_{\delta}$) layers is much longer ($d_{\text{Hg-O}_{\text{eq}}}$ ≈ 2.7 Å). Thus, the Hg–O$_{\text{eq}}$ bond is weaker than Hg–O$_{\text{ap}}$ and has no serious influence on the commensurability between (BaO) layers and (HgO$_{\delta}$) layers.

The charge criterion assumes, first, electroneutrality of the entire structure and, second, that adjacent layers should not have big charges of the same sign.

Conducting (CuO₂) layers have negative charge, which can be partially compensated by positively charged (Ca$^{2+}$) layers. (HgO$_{\delta}$) layers are also positively charged, and can therefore, likewise, compensate the negative (CuO₂) layers. As mentioned above, the Hg–O$_{\text{eq}}$ bond in the (HgO$_{\delta}$) layer is comparatively weak, which means that an oxygen anion$^1$ surrounded by four adjacent mercury cations can be removed rather easily, for instance, during heat treatment. Changing the concentration ($\delta$) of this oxygen evidently results in a change of the whole (HgO$_{\delta}$) layer charge, so that an increase in $\delta$ leads to a decrease in the positive (HgO$_{\delta}$) layer charge. In this situation (in order to retain electroneutrality of the entire structure), the total charge of another layer should increase, and there is only one possibility for this: raising the (CuO₂) layer charge by means of a copper oxidation state ($v_{\text{Cu}}$) increase.

Another possibility of changing the copper oxidation state is a partial replacement of Hg$^{2+}$ cation (or Ba$^{2+}$) by another, more highly, charged cation, for instance, Tl$^{3+}$. In this case the total charge of the (HgO$_{\delta}$), or (BaO), layer will increase, and the (CuO₂) layer charge will decrease due to $v_{\text{Cu}}$ decrease.

It is clear that changes of insulating slab charge result in changes of $v_{\text{Cu}}$ or, in other words, the number of charge carriers in the conducting block. That is why an insulating slab is often called a charge reservoir.

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$^1$ This O$^{2-}$ is also referred to as an extra-oxygen anion.
I.2.3. Four-digit abbreviation system

Chemical formulas of compounds related to the family of Hg-based superconducting copper oxides (as well as formulas for many others high-\(T_c\) cuprate superconductors) are quite lengthy and complicated. The use of a special four-digit abbreviation system instead of ordinary formulas has therefore been suggested, for reasons of simplicity.

According to this scheme one should only indicate a cation from a charge reservoir block (\(i.e.\) Hg in the case of Hg-based superconductors) and then, after a hyphen, four digits corresponding to the number of each cation per unit cell in the following order:

1) number of cations per unit cell in the charge reservoir block;
2) number of cations per unit cell in separating layers between conducting and charge-reservoir blocks (\(i.e.\) Ba in the case of Hg-based superconductors);
3) number of cations per unit cell in layers separating the (CuO\(_2\)) layers (\(i.e.\) Ca);
4) number of copper cations per unit cell in (CuO\(_2\)) layers.

Thus, the formula of the first member of Hg-based superconducting cuprates (HgBa\(_2\)CuO\(_{4+\delta}\)) will be Hg-1201 (zero here corresponds to an absence of any particular atom). Another example is the formula of one of the earliest discovered high-\(T_c\) cuprate superconductors, the well known “123 phase” (YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) or Y-123). According to this system its formula should be written as Cu-1212.

The same scheme is also applied to the general formulas of homologous series: for instance, the formula of one-layer Hg-based superconducting cuprates (HgBa\(_2\)Ca\(_{n-1}\)Cu\(_n\)O\(_{2n+2+\delta}\)) will be Hg-12(n-1)n, where Latin letters denote possible different number of atoms per unit cell.

This system is now very common in the scientific literature, focused on high-\(T_c\) superconductors studies, and will also be used in the present thesis.
1.2.4. General crystal structure description

The crystal structures of all compounds from the homologous series of Hg-based superconducting cuprates adopt tetragonal symmetry (space group: \(P4/mmm\)). *Figure 3 a, b and c* displays crystal structures of the first three members of the series.

*Figure 3*. Representation of Hg-1201 (a), Hg-1212 (b) and Hg-1223 (c) crystal structures. Available layers and atomic positions are marked.

The coordination polyhedron of copper in Hg-1201 is an octahedron (CN = 6); in Hg-1212 it is a tetragonal pyramid (CN = 5), but starting from the third member in the series there are two distinct crystallographic positions for copper atoms in the structure, with two different polyhedra, namely: tetragonal pyramid (CN = 5) and square (CN = 4).

The (CuO₂) layers are almost flat for the first two members of the series (\(\angle O–Cu–O \approx 180^\circ\)). In Hg-1223 the “internal” (CuO₂) layer consists of flat squares, while the “external” (CuO₂) layers, constructed from the bases of tetragonal pyramids, are slightly buckled (\(\angle O–Cu–O \approx 178^\circ\)). It should be emphasized that the distortion of the external (CuO₂) layers increases with increasing \(n\) (i.e. number of (CuO₂) planes).

The tetragonal unit cell parameters change simultaneously with \(n\): the \(a\) parameter decreases, whereas the \(c\) parameter obviously increases. The largest \(a\) parameter change occurs between the first two members of the series: Hg-1201 (\(a \approx 3.880\) Å) and Hg-1212 (\(a \approx 3.856\) Å). The difference between the second and the third member (\(a \approx 3.852\) Å) is insignificant. Further on, the value of \(a\) almost ceases to change and equals: \(a \approx 3.850–3.852\) Å. The \(c\) parameter change (with increasing \(n\)
obviously parallels the increase in number of (CuO_2) layers or, to be exact, the increase in conducting block thickness.

As already mentioned, the existence of an extra oxygen anion in the (HgO_δ) layer is one of the specific features of Hg-based cuprates crystal structure. This anion is weakly connected to adjacent Hg^{2+} and Ba^{2+} cations (d_{Hg-O_δ} ≈ 2.73 Å; d_{Ba-O_δ} ≈ 2.83 Å) thus opening a possibility to change δ over a wide range. It should be noted that the δ value is directly associated with the average oxidation state of copper (v_{av Cu}). Assuming v_{Hg} = v_{Ba} = v_{Ca} = +2, v_{O} = −2, and also taking the electroneutrality principle into account, one can obtain for Hg-based superconducting cuprates the following correlations between δ and v_{av Cu}:

\[
v_{av Cu} = \frac{2}{n} \times (n + \delta) \tag{2}
\]
\[
\delta = \frac{(v_{av Cu} \times n - 2n)}{2} \tag{3}
\]

It was found that a change of δ (or v_{av Cu}) affects the T_c value, and the T_c(δ) dependence of each homologue has a cupola-shaped character (Figure 4). The highest T_c value (or T_{c, max}) corresponds to the so-called optimal value of δ (or δ_{opt}). An increase (as well as decrease) in extra-oxygen content leads to T_c reduction, down to the total loss of superconductivity. Therefore, each particular sample, depending on its δ value may be either in underdoped (U.D.), optimally doped (Opt.D.) or overdoped state (Ov.D.). It should be noted that δ_{opt} values grow with increasing n.

The T_{c, max}(n) dependence for Hg-based cuprates has a parabolic shape as well (see Figure 5). T_{c, max} values increase from Hg-1201 (T_{c, max} = 97 K) to Hg-1212 (T_{c, max} = 127 K) and finally reach their maximum for the Hg-1223 (T_{c, max} = 135 K). Starting from the fourth member of the series, the T_{c, max} values go down (e.g. for Hg-1234: T_{c, max} = 126 K; for Hg-1245: T_{c, max} = 110 K; for Hg-1256: T_{c, max} = 100 K etc.). An observed T_{c, max} decrease for higher homologues was recently explained as a result of insufficient charge carrier concentration, in other words, that investigated

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\(^1\) Different (CuO_2) layers could exhibit different values of ν_{Cu}. Thus, an average value (v_{av Cu}) is often used for simplicity.
samples were in fact underdoped. However, synthesis of Hg-1234 and Hg-1245 samples in overdoped state [1] refuted this hypothesis. It was instead suggested that the reason for the $T_{c, \text{max}}$ decrease in higher homologues is found in structural features of studied phases: particularly, it could be related to increase of external (CuO$_2$) layer distortion.

The lattice constants, $\delta$ and $T_c$ values for Hg-1201, Hg-1212 and Hg-1223 samples obtained by different research groups are summarized in Tables 1–3:

**Table 1.**

<table>
<thead>
<tr>
<th>lattice constants</th>
<th>$\delta$ (method of determ.)</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.87766(4)</td>
<td>9.5073(1)</td>
<td>0.08(2) (IT)</td>
<td>94</td>
</tr>
<tr>
<td>3.8887(5)</td>
<td>9.540(2)</td>
<td>0.01(1) (IT)</td>
<td>68</td>
</tr>
<tr>
<td>3.8818(5)</td>
<td>9.525(2)</td>
<td>0.08(1) (IT)</td>
<td>94</td>
</tr>
<tr>
<td>3.8806(6)</td>
<td>9.525(2)</td>
<td>0.08(1) (IT)</td>
<td>95</td>
</tr>
<tr>
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</table>

*IT: iodometric titration; ND: neutron diffraction; XRD$^a$: X-ray powder diffraction; XRD$^a$ single crystal diffraction; NS: non superconducting.*
Table 2.
Lattice constants, δ and $T_c$ values obtained for different Hg-1212 samples.

<table>
<thead>
<tr>
<th>lattice constants</th>
<th>δ (method of determ.)$^a$</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
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<tr>
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</table>

$^a$ XRDP: X-ray powder diffraction; ND: neutron diffraction.

Table 3.
Lattice constants, δ and $T_c$ values obtained for different Hg-1223 samples.

<table>
<thead>
<tr>
<th>lattice constants</th>
<th>δ (method of determ.)$^a$</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
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<td>15.8476(7)</td>
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<td>3.8860(5)</td>
<td>15.887(3)</td>
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<td>0.18(4) (ND)</td>
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</tbody>
</table>

$^a$ ND: neutron diffraction; IT: iodometric titration; XRDS: X-ray single crystal diffraction.

Thus, from the structural point of view, there are still several problems concerning these homologues, mainly caused by observed discrepancies in $\delta_{opt}$ values. It should be noted that precise structural studies of these compounds are normally obstructed by sample quality (presence of impurities), which casts doubt on some of the data presented above. Differences in phase compositions, presence of amorphous impurities, formation of microstructure defects etc.: these are some the factors that cause variations in experimentally obtained or calculated $\delta_{opt}$ values. That is why an understanding of how synthesis conditions influence the structure and properties of obtained samples seems to be quite important.
1.2.5. Doping of Hg-based cuprates by charge carriers

Hg-based superconductors, as well as many other high-$T_c$ cuprates, are compounds with hole-type conductivity. Holes ($h$) could be formed, for instance, in the following process:

$$O \rightarrow O^{2-} + 2h$$ \hspace{1cm} (4)

This process occurring in the charge reservoir block corresponds to $\delta$ increase or, in other words, decrease of $(\text{HgO}_\delta)$ layer charge. In this situation, the charge of $(\text{CuO}_2)$ layers should increase due to $\nu_{\text{av Cu}}$ increase:

$$\text{Cu}^{2+} + h \rightarrow \text{Cu}^{3+}$$ \hspace{1cm} (5)

Thus, charge carriers are transferred from the charge reservoir into the conducting block.

It is obvious that extra-oxygen content ($\delta$) or doping level determines the hole concentration ($p$). The relationship between $\delta$ and $p$ could be different depending on the doping mechanism.

The ionic model of doping seems to be the most simple and intuitive from the chemical point of view. Incorporation of every extra-oxygen anion according to this model is followed by formation of two holes (Equation 4) or, in other words:

$$p = 2 \times \delta$$ \hspace{1cm} (6)

Extensive experimental data are in agreement with this model [4, 8, 12, 18, 24–26].

However, some results [27, 28, 29] could be explained only by the assumption that extra-oxygen anion incorporation results in formation of one hole only (i.e. $p = \delta$):

$$O \rightarrow O^- + h$$ \hspace{1cm} (7)

It has been supposed that, according to presented scheme (Equation 7), $O^-$ anions should exist in the structure [27, 28]. Another possible explanation of the $p$ value could be rather strong covalent interaction between mercury and the extra oxygen ions. Theoretical calculations confirming this assumption are given, for instance, in [30]. One should also take into consideration that various defects can exist in the crystal structure of Hg-based cuprates. The presence of these defects could formally result in an increase of $\delta$, while at the same time $p$ remains constant (for instance, in isovalent substitution of carbonate $\text{CO}_3^{2-}$ groups for $\text{HgO}_2^{2-}$ fragments).
It should be noted that description of the doping mechanism is simpler in the case of the first member (Hg-1201) since it contains only one (CuO$_2$) layer and consequently only one type of copper atoms in the structure. For Hg-1212 (two (CuO$_2$) layers and one type of copper atom) and Hg-1223 (three (CuO$_2$) layers and two types of copper atom) the real doping mechanism could be more complicated, especially if one adopts an idea about uneven distribution of charge carriers among nonequivalent \textit{i.e.} internal, external (CuO$_2$) planes.
CHAPTER 3.
SYNTHESIS OF Hg-BASED CUPRATES

I.3.1. General remarks about synthesis of Hg-based cuprates

Much work has been devoted to the task of synthesizing Hg-based cuprates. However, this problem is still not satisfactorily solved, mainly because of synthesis process difficulties. It has only been possible to obtain the Hg-1201 phase without impurities [3, 31]. All Ca-containing homologues are normally obtained as multi-phase samples; the number (and quantity) of admixtures increasing with n. Another serious problem, which is especially crucial for synthesis of higher homologues (n ≥ 2), is reproducibility: i.e. different samples obtained under almost identical conditions may contain different amounts of impurity phases.

The red modification of mercury (II) oxide (HgO) is normally used for the synthesis of Hg-based cuprates. This compound has low thermal stability and decomposes during heating at rather low temperatures with formation of mercury and oxygen gas. At the same time, synthesis of Hg-based cuprates at these low temperatures is kinetically hindered. Therefore, usage of an ordinary flow-type reactor is not suitable in this case, since Hg will evaporate from the reaction mixture before reaction with other oxides. That is why synthesis is normally carried out in a closed volume: for instance, in silica tubes or under high pressure. Using a closed vessel is also desirable because of the high toxicity of several Hg-containing compounds, and especially liquid mercury.

It should be mentioned that the first three members of the Hg-based homologous cuprate series can be obtained using either sealed tubes or high pressure, whereas higher homologues (n ≥ 4) are normally only synthesized under high pressure.

I.3.2. Synthesis in sealed silica tubes

Synthesis in sealed silica tubes is preferably used for preparation of the first three members of the Hg-based homologous series since this method is much simpler than high-pressure techniques, and does not require special expensive facilities.

A mixture of simple oxides (Equation 8) or a precursor with the nominal starting composition “Ba$_2$Ca$_{n-1}$Cu$_n$O$_z$” is normally used for the synthesis (Equation 9):

\[
\text{HgO + 2 BaO + (n-1) CaO + n CuO \rightarrow HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \quad (8)
\]

\[
\text{HgO + Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z \rightarrow HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta} \quad (9)
\]

There are several ways to prepare precursors:
• from nitrates or nitrates and oxides: Ba(NO₃)₂, Ca(NO₃)₂×4H₂O (or CaO), Cu(NO₃)₂×3H₂O (or CuO), which are decomposed in vacuum at 500–550°C or in a flow of oxygen at 900–950°C [32–34].
• from a mixture of carbonates: (BaCO₃), (CaCO₃) and copper oxide (CuO), preliminarily annealed at 900–1000°C [35].
• from metal oxides and peroxides at 500–600°C [36, 37].
• from nitrates using cryochemistry methods [37, 38].
• using the sol–gel method [39, 40].

The main advantage of using a precursor is its enhanced stability towards CO₂ and moisture in the air. One should also take into account that the initial components in the precursor are better homogenized than in an oxide mixture. The maximal homogenization can be achieved with the cryochemical and sol–gel methods. The main drawback of using a precursor is its relatively low kinetic activity. This may be explained by the fact that a precursor is normally a well-crystallized product after preliminary annealing at 600–900°C. For instance, Hg-1223 samples were obtained from a mixture of metal oxides at 860°C during 6 h, while using a precursor required a synthesis time up to 24 h [41]. Moreover, a precursor obtained from carbonates could be contaminated with carbon (or C-containing admixtures), which may result in formation of oxycarbonates [42]. Synthesis from oxide- (or peroxide-) precursors encounters the same problems as synthesis from a mixture of metal oxides.

A mixture of oxides is more sensitive to CO₂ and moisture than a precursor, mainly because of the presence of BaO. Therefore all operations with initial components should be carried out in special dry boxes in inert gas or N₂ atmosphere. An oxide mixture is kinetically more active than a precursor mixed with HgO, and the best samples of Ca-containing homologues (i.e. with a maximal yield of the intended superconducting phase) have consequently been obtained utilizing the synthesis from oxide mixtures [15, 16, 43–45].

The presence of impurity phases in the final solid product may be explained not only by contamination of initial reagents. The obtained phase composition in fact depends on a number of factors. Some impurities can be formed during the synthesis, for instance, barium cuprates (BaₓCuᵧO₂₊δ) and/or mercurates of calcium (CaHgO₂) and/or barium (BaHgO₂); other homologues of the series (usually lower ones in a case of any higher homologue (n ≥ 2) synthesis). Sometimes one may observe remaining amounts of unreacted starting oxides (CuO or CaO). Finally, it is necessary to take into account that several compounds (for instance, BaO) are noticeably volatile at high temperatures, which may result in reaction with the silica tube walls.
High activity of some synthesis components imposes rigid requirements on the choice of tube and crucible\(^1\) material. Silica (SiO\(_2\)) or alumina (Al\(_2\)O\(_3\)) tubes are usually used for this purpose. Tubes and crucibles made of other materials often do not satisfy to all necessary requirements for high-\(T_c\) cuprate synthesis (i.e. stability at \(T \approx 900–1000^\circ C\) during 10–30 h etc.) or react significantly with substances present in a tube (e.g. could be oxidized during synthesis, react with BaO etc.). Evidently, these side-reactions may result in uncontrollable change in cation composition of the solid phase obtained and also in tube destruction (e.g. crack formation or explosion). A certain role is also played by availability (and cost) of potential tube/container material (for instance, Au).

1.3.3. Optimization of synthesis process in sealed silica tubes

HgO decomposes on heating, as mentioned above, so that mercury first passes from solid into gas phase and then starts reacting with the solid precursor (or oxide mixture). It should be noted that significant amounts of mercury might remain in the gas phase in equilibrium with the solid phase, upon termination of reaction. Therefore, metallic mercury could be formed during tube cooling (or quenching) and this fact seriously influences both the cation composition of the obtained solid phase and the phase composition of the solid product. That is why optimization of the synthesis process is necessary (i.e. empirical investigation of different factors determining cation and phase composition). The parameters varied are mass and cation composition of the initial mixture, temperature \(T\) and synthesis duration \(t\), inner free volume of a tube, cooling conditions etc. Oxygen partial pressure \(p\{O_2\}\) inside a tube is also crucial, since a change in this parameter will result in alteration of mercury partial pressure \(p\{Hg\}\) and therefore final solid product composition.

A synthesis with controlled oxygen partial pressure was carried out first as a two-temperature synthesis of the Hg-1201 phase [31] (see Figure 6a) followed by a three-temperature synthesis of Hg-1201 [3] (see Figure 6b), which allowed simultaneous oxygen and mercury partial pressure control. In both techniques Ba\(_2\)CuO\(_{3+y}\) and HgO were placed at the low-temperature end of the tube. The transition-metal oxide mixture (CoO/Co\(_3\)O\(_4\), Mn\(_2\)O\(_3\)/MnO\(_2\) or CuO/Cu\(_2\)O) was at the other end of the tube, corresponding to the high-temperature zone. An excess of this mixture was used as oxygen getter: a certain partial oxygen pressure was realized above it, depending on temperature. The partial pressure of mercury was controlled with a mercury getter: i.e. a mixture of Hg-1201 and Ba\(_2\)CuO\(_{3+y}\) placed at the temperature \(T_2\) [3] (see Figure 6b). Using these synthesis techniques allowed for the first time a reproducible synthesis of samples containing only the Hg-1201 phase.

\(^1\) A crucible is often used as an additional tool, preventing direct contact between reaction mixture and tube walls.
Synthesis of Ca-containing homologues is more complicated than that of Hg-1201, normally requiring much longer annealing times and yielding a final product that contains some admixtures. The main reasons for this fact are summarized in [46]:

1. There is no stable compound that could be used as a precursor together with HgO, such as Ba$_2$CuO$_{3+y}$ in case of Hg-1201. A mixture of phases is usually utilized in order to obtain Hg-1212 or Hg-1223, which obviously causes a problem of impurity formation and also prolongation of synthesis time, for instance, due to diffusion of synthesis components.

2. It has been suggested that synthesis of higher homologues proceeds through a stage of formation of lower homologues. This fact could result in increase of synthesis time as well.

3. The equilibrium partial mercury pressure over Hg-1212 (or over Hg-1223) is significantly higher than over Hg-1201: for instance, Hg-1212 has $p$(Hg) = 18 atm at 800°C, while for Hg-1201 it is only 2 atm at the same temperature [47].

4. Possibility of CaHgO$_2$ and BaHgO$_2$ formation. These compounds are stable at certain values of $p$(Hg), $p$(O$_2$) and $T$.

Unfortunately, a detailed investigation of the $p$(Hg)–$p$(O$_2$)–$T$ relationships in the Hg–Ba–Ca–Cu–O system is not yet complete, and therefore exact knowledge of the stability regions of Hg-1212 and Hg-1223 is not available. That is why that empirical circumstances conditions found by various scientists cannot be definitely established as equilibrium conditions.
Optimization of Hg-based cuprates synthesis could also be performed with the use of various additives (or fluxes). A flux is a substance, added during one of the synthesis steps (usually mixing of initial reagents), which influences the chemical reactions proceeding in the system, and which is finally removed somehow from the reaction mixture. For different high-$T_c$ cuprates it was shown that the use of such additives under similar conditions may result in: 1) synthesis of samples with higher content of required superconducting phase and less impurities in the final product; 2) formation of well-crystallized samples; 3) essential reduction of synthesis time and temperature; 4) improvement of several microstructural characteristics etc.

$\text{Na}_2\text{CO}_3$ and $\text{K}_2\text{CO}_3$ were used as fluxes for synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ in one of the first investigations in this area [48]. These fluxes were mixed with a nitrate precursor before synthesis and were then washed out of the final solid product. It was shown that using $\text{Na}_2\text{CO}_3$ results in formation of samples with a high content of $\text{YBa}_2\text{Cu}_4\text{O}_8$ with rather high $T_c = 77$ K. It was even possible to omit the washout step because of decomposition of the carbonate into volatile $\text{Na}_2\text{O}$ and $\text{CO}_2$ so that the flux evaporated [49]. Several groups attempted to use alkali metal nitrates [50], $\text{Na}_2\text{O}_2$ [51] etc. instead of carbonates to avoid possible carbon contamination of the synthesized compounds. The influence of a large spectrum of fluxes (including various fluorides: $\text{PbF}_2$, $\text{NaF}$, $\text{LiF}$ etc.) on the synthesis of high-$T_c$ superconducting Y-124 is reported in [52, 53]. It was found that using lithium fluoride yielded samples with a high content of the desired superconducting phase. The positive influence of an LiF flux on the synthesis and properties of Pb-doped Bi-2223 samples was also reported [54].

The possibility of side reactions, both promoted by the flux and with participation of this additive, can be seen as the main disadvantages of the flux method. The opportunity of cation and/or anion incorporation into the structure of the synthesized phase is another problem that should be taken into consideration. Different types of substitutions, influencing both structure and properties, are rather common in Hg-based cuprates (see, for instance, [42, 55, 56]). Therefore the flux should be selected very carefully, considering all these problems.

With LiF one can expect substitution of $\text{Li}^+$ for $\text{Cu}^{2+}$ and also fluoride anion incorporation and/or possibly substitution of fluorine for oxygen. Besides, an addition of solid fluoride into the initial reaction mixture might result in formation of thermodynamically stable fluorides (for instance, $\text{BaF}_2$ or $\text{CaF}_2$).
CHAPTER 4.
SUBSTITUTIONS IN Hg-BASED CUPRATES

I.4.1. Introduction

Crystal structure modification via substitution of some atoms (or cations/anions) for others is a common method, widely used in many systems of superconducting cuprates. Usually there are in any particular structure several different atoms that could be mutually or separately replaced by others. It is evident that the choice of substituent atoms is rather broad, thus opening a wide area for search of new modified compounds. Investigation of particular atomic substitution limits might also be interesting. A change of structural parameters as a result of substitution obviously influences the electronic structure and various physical characteristics of cuprates, thus being of both fundamental and practical interest.

The existence of structures with different types of substitution is typical for Hg-based cuprates. Substitution of copper for mercury and carbon for mercury are two of the most common examples. Both of these substitutions may be considered “unintentional,” because copper is always present among the synthesis components, and carbon may also be present in the initial reaction mixture (for instance, in anion groups of C-containing precursors: carbonates, oxalates etc.). Further investigation showed that other types of substitution are also possible in Hg-based cuprates: for instance, Tl\(^{3+}\) for Hg\(^{2+}\), Sr\(^{2+}\) for Ba\(^{2+}\), F\(^{-}\) for O\(^{2-}\) etc.

Many investigations of substituted compounds have been focused mainly on structure–property relationship, particularly on the influence of different structural factors on \(T_c\). A basis for many of the experiments performed consisted in simulation of an external pressure effect. It is well known that Hg-based cuprates at high pressures show enhanced \(T_c\) values, which are notably higher than at normal pressure. For instance, the record \(T_c \approx 164\) K was established for Hg-1223 at \(P = 31\) GPa [57]. An observed \(T_c\) increase was explained from a structural point of view by strong compression of the crystal structure. However, a corresponding decrease of lattice parameters could be achieved by purely chemical means, namely via substitutions. This chemical compression effect is clearly shown, for instance, by the substitution of Sr\(^{2+}\) for Ba\(^{2+}\).

I.4.2. Substitutions of cations

In principle, it is possible to imagine substitution of any cation in the structure of Hg-based cuprates. However, one should realize that any changes in conducting (CuO\(_2\)) layers or adjacent (Ca \(_{\text{Cu}}\)) ones usually have a very negative influence on the superconducting characteristics (for instance, \(T_c\) lowering or even entire loss of superconductivity). From this point of view, the influence of substitutions in the insulating block seems to be less crucial. Moreover, several
compounds with this type of substitution reveal some improved characteristics compared to non-substituted analogues.

I.4.2.1. Structures with a partial substitution of mercury cations

Replacement of a mercury cation $\text{Hg}^{2+}$ by another $M^{z+}$ can be performed quite easily, because of the large $\text{Oap–Hg–Oap}$ distance ($\approx 4 \text{ Å}$) and also because of the fact that extra oxygen anions, located at a distance of $\approx 2.7 \text{ Å}$, do not appreciably hinder incorporation of cation substituents.

Structural distortions caused by different cation substitutions of $M^{z+}$ for $\text{Hg}^{2+}$ are schematically represented in Figure 7 a–c. Usually, the coordination numbers of $\text{Hg}^{2+}$ (CN = 2) and the cation substituent $M^{z+}$ are different. Therefore, incorporation of an $M^{z+}$ cation is followed by insertion of additional extra oxygen anions required for its coordination. These additional anions occupy positions on the edge between $\text{Hg}^{2+}$ and $M^{z+}$ cations, if the $M^{z+}$ cation requires square or octahedral coordination (Figure 7 a). The most appropriate example in this case is a partial substitution of copper for mercury, studied in many instances for Hg-1201 [58–60], Hg-1212 [19, 61] and Hg-1223 [19, 22, 23, 41]. Replacement of mercury by cations with tetrahedral or trigonal coordination normally results in more severe crystal structure distortions (Figure 7 c). Extra oxygen anions in this case shift more strongly towards the $M^{z+}$ cation, therefore this type of substitution is
often described in the literature as a substitution of an $MO_{2}^{2-}$ anion group for the whole $HgO_{2}^{2-}$ fragment. As an example, on may take substitution of trigonal carbonate $CO_{3}^{2-}$ [5, 42] or tetrahedral sulfate group $SO_{4}^{2-}$ [56] for the $HgO_{2}^{2-}$ dumbbell.

Recently, it has been shown that partial replacement of $Hg^{2+}$ by $Pb^{2+}$ or $Tl^{3+}$ cations in $Hg$-1223 result in formation of compounds with record-high $T_c$ values (> 135 K) (see, for instance, [62, 63]). A possibility of obtaining samples with $T_c > T_{c, \text{max}}$ initiated intensive studies focused on substitution of various atoms ($Tl$, $Pb$, $V$, $Mo$, $Cr$, $Ti$, $Bi$, $Re$ etc.) for mercury in the structures of $Hg$-1223 and lower homologues. Lattice parameters and $T_c$ values of various substituted $Hg$-1201, $Hg$-1212 and $Hg$-1223 samples are summarized in Tables 4–6 (corresponding values for non-substituted compounds obtained in [55] are given in the tables for comparison).

Table 4.

Lattice parameters and $T_c$ values of $(Hg_{1-x}M_x)Ba_2CuO_{4+\delta}$ compounds.

<table>
<thead>
<tr>
<th>composition$^a$</th>
<th>lattice parameters</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>$HgBa_2CuO_{4+\delta}$</td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td></td>
</tr>
<tr>
<td>$(Hg_{0.8}V_{0.2})Ba_2CuO_{4.3}$</td>
<td>3.8863(3)</td>
<td>9.338(1)</td>
<td>96</td>
</tr>
<tr>
<td>$(Hg_{0.8}Mo_{0.1})Ba_2CuO_{4.2}$</td>
<td>3.8748(3)</td>
<td>9.435(1)</td>
<td>75</td>
</tr>
<tr>
<td>$(Hg_{0.75}Mo_{0.25})Ba_2CuO_{4.4}$</td>
<td>3.8819(3)</td>
<td>9.378(1)</td>
<td>74</td>
</tr>
<tr>
<td>$(Hg_{0.9}W_{0.1})Ba_2CuO_{4.2}$</td>
<td>3.8746(3)</td>
<td>9.450(1)</td>
<td>89</td>
</tr>
<tr>
<td>$(Hg_{0.75}W_{0.25})Ba_2CuO_{4.4}$</td>
<td>3.8713(3)</td>
<td>9.416(1)</td>
<td>45</td>
</tr>
<tr>
<td>$(Hg_{0.6}Cr_{0.4})Ba_2CuO_{4.1}$</td>
<td>3.9261(3)</td>
<td>9.306(1)</td>
<td>NS$^b$</td>
</tr>
<tr>
<td>$(Hg_{1-x}Bi_x)Ba_2CuO_{4+\delta}$</td>
<td>3.8800(4)</td>
<td>9.492(2)</td>
<td>75</td>
</tr>
<tr>
<td>$(Hg_{0.9}Ce_{0.1})Ba_2CuO_{4+\delta}$</td>
<td>3.885</td>
<td>9.530</td>
<td>97</td>
</tr>
<tr>
<td>$(Hg_{0.85}Ce_{0.15})Ba_2CuO_{4+\delta}$</td>
<td>3.8801(2)</td>
<td>9.495(1)</td>
<td>90</td>
</tr>
<tr>
<td>$(Hg_{0.85}Pr_{0.15})Ba_2CuO_{4+\delta}$</td>
<td>3.8800(4)</td>
<td>9.495(1)</td>
<td>81</td>
</tr>
<tr>
<td>$(Hg_{0.9}Nd_{0.1})Ba_2CuO_{4+\delta}$</td>
<td>3.8875(2)</td>
<td>9.516(1)</td>
<td>76</td>
</tr>
</tbody>
</table>

$^a$ cation composition according to EDX data; $^b$ non-superconducting.
Table 5. Lattice parameters and $T_c$ values of $(\text{Hg}_{1-x}\text{M}_x)\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compounds.

<table>
<thead>
<tr>
<th>composition$^a$</th>
<th>lattice parameters</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HgBa}_2\text{CaCu}<em>2\text{O}</em>{6+\delta}$</td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td></td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.8}\text{V}</em>{0.2})\text{Ba}_2\text{Ca}_2\text{Cu}<em>2\text{O}</em>{6.3}$</td>
<td>3.8624(3)</td>
<td>12.704(1)</td>
<td>117</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.75}\text{Mo}</em>{0.25})\text{Ba}_2\text{CaCu}<em>2\text{O}</em>{6.4}$</td>
<td>3.8692(3)</td>
<td>12.500(1)</td>
<td>119</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.9}\text{W}</em>{0.1})\text{Ba}_2\text{CaCu}<em>2\text{O}</em>{6.2}$</td>
<td>3.8602(3)</td>
<td>12.576(1)</td>
<td>127</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.75}\text{W}</em>{0.25})\text{Ba}_2\text{Ca}_2\text{Cu}<em>2\text{O}</em>{6.4}$</td>
<td>3.8607(3)</td>
<td>12.661(1)</td>
<td>118</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.8}\text{Ti}</em>{0.2})\text{Ba}_2\text{CaCu}<em>2\text{O}</em>{6.2}$</td>
<td>3.8568(3)</td>
<td>12.581(1)</td>
<td>127</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.6}\text{Cr}</em>{0.4})\text{Ba}_2\text{Ca}_2\text{Cu}<em>2\text{O}</em>{6.1}$</td>
<td>3.8753(3)</td>
<td>12.488(1)</td>
<td>110</td>
</tr>
</tbody>
</table>

$^a$ cation composition according to EDX data.

Table 6. Lattice parameters and $T_c$ values of $(\text{Hg}_{1-x}\text{M}_x)\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compounds.

<table>
<thead>
<tr>
<th>composition$^a$</th>
<th>lattice parameters</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HgBa}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8+\delta}$</td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td></td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.7}\text{Pb}</em>{0.3})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8.45}$</td>
<td>3.8564(3)</td>
<td>15.856(1)</td>
<td>105</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.8}\text{Ti}</em>{0.2})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8+\delta}$</td>
<td>3.8457(1)</td>
<td>15.8252(7)</td>
<td>135</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.7}\text{V}</em>{0.3})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8.3}$</td>
<td>3.8574(5)</td>
<td>15.794(2)</td>
<td>138</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.75}\text{Mo}</em>{0.25})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8.4}$</td>
<td>3.8629(3)</td>
<td>15.652(1)</td>
<td>120</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.7}\text{Ti}</em>{0.3})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8.4}$</td>
<td>3.8537(3)</td>
<td>15.731(1)</td>
<td>129</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.7}\text{V}</em>{0.3})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8.4}$</td>
<td>3.8507(3)</td>
<td>15.707(1)</td>
<td>128</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.6}\text{Cr}</em>{0.4})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8.1}$</td>
<td>3.8631(3)</td>
<td>15.625(1)</td>
<td>95</td>
</tr>
<tr>
<td>$(\text{Hg}<em>{0.8}\text{Au}</em>{0.2})\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8+\delta}$</td>
<td>3.8646(2)</td>
<td>15.739(1)</td>
<td>131</td>
</tr>
<tr>
<td>$(\text{Hg}_{1-x}\text{Re}_x)\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{8+\delta}$</td>
<td>3.8865(1)</td>
<td>15.2126(5)</td>
<td>132</td>
</tr>
</tbody>
</table>

$^a$ cation composition according to EDX data.

Presented values of lattice parameters confirm that substitution always results in some distortion of the structure. The most significant changes occur in the $c$ parameter, caused by the difference in apical Hg–O and $M$–O distances, while the $a$ parameter changes are not that obvious. That is why the observed structure compression resulting from chemical substitution is different from the effect of high pressure, which is a substantial decrease of both tetragonal lattice parameters.

It is possible to follow the influence of substitutions on $T_c$ value for the obtained substituted compounds. A correlation could be observed comparing the $T_c$ values with the *structural anisotropy* ($c/a$). The value of $c/a$ is maximal in the non-substituted Hg-1201 phase ($\approx 2.456$). Incorporation of
a cation substituent results in $c/a$ decrease from $≈ 2.439$ \{for (Hg,W)-1201\} to $≈ 2.370$ \{for (Hg,Cr)-1201\} (see Table 4) followed by corresponding change in $T_c$ values: $T_c = 91$ K for Hg-1201 and 89 K for (Hg,W)-1201, while (Hg,Cr)-1201 is non-superconducting. Similar correlations can be also found for Hg-1212, Hg-1223 and their substituted analogues.

Another problem that should be mentioned here is the existence of a solubility limit or maximal amount of a cation substituent ($x$) per unit cell. Investigation of substituted compounds, or solid solutions, with the nominal composition (Hg$_{1-x}$M$_x$)Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ suggested, that the solubility limit cannot be higher than $≈ 20$–$25\%$. It was shown that synthesis of Hg-based cuprates from initial mixtures containing larger amounts of cation substituent ($x > 0.3$) normally results in formation of additional impurity phases. This fact could be explained, for instance, by the impossibility of introducing two adjacent MO$_x$ groups, due to their mutual electrostatic repulsion. Steric factors, hindering further substitution, also seem to be crucial, especially for large MO$_x$ fragments. There are some discrepancies in the literature concerning observed $T_c(x)$ dependencies for different obtained solid solutions. For instance, investigation of (Hg$_{1-x}$Pbx)-1223 solid solutions revealed a cupola-shaped $T_c(x)$ dependence [69], which was explained by possible overdoping of the compounds with high $x$ values. Studies of Mo- and W-substituted Hg-1201 phases revealed a linear $T_c(x)$ dependence [55].

I.4.2.2. Structures with a partial substitution of barium cations

Successful synthesis of HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ compounds initiated a search for their Sr-containing analogues with partial \{Hg(Ba$_{1-x}$Sr$_x$)$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$\} or full \{HgSr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$\} substitution of Sr$^{2+}$ for Ba$^{2+}$. It was found that Hg$_2$(Ba$_{1-x}$Sr$_x$)$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ solid solutions could be obtained only in the Hg-1201 phase (see, for instance, [70]). Attempted syntheses of similar solid solutions of other homologues were not successful. However, it was shown that it is possible to stabilize these phases by simultaneous substitution of one or several other cations in the structure.

Substitution of Sr$^{2+}$ for Ba$^{2+}$ should also result in chemical compression of the structure (the cationic radii of Sr$^{2+}$ and Ba$^{2+}$ are 1.25 Å and 1.47 Å, respectively) thus simulating an external pressure effect. The observed structure compression is even more prominent in this case, compared to partial replacement of Hg$^{2+}$ by other cations. Nevertheless, analysis of many experimental data established that the chemical compression caused by substitution of Sr$^{2+}$ for Ba$^{2+}$ always results in a significant decrease of $T_c$. It seems that the distortion of the conducting (CuO$_2$) layers during this substitution is more important than the chemical compression effect.

---

1 It is possible to suggest partial substitution of Cr for Cu in the structure of (Hg,Cr)-1201, which results in a drastic $a$-parameter change (see Table 4) and therefore in superconductivity loss.
Thus, partial or full substitution of Sr\(^{2+}\) for Ba\(^{2+}\) does not seem promising for the aim of \(T_c\) increase. However, compounds with this type of substitution can exhibit other improved characteristics, for instance, enhanced \(H_{irr}\) values [71].

**1.4.3. Substitutions of anions**

Oxygen anions could also be replaced by other anions, for instance, halogenide anions (F\(^-\), Cl\(^-\) etc.). Compounds with partial substitution of fluorine for oxygen have been studied more intensively among all of them. Substitution of F\(^-\) for O\(^2-\) is made possible by the similarities in crystal chemistry of these anions (anionic radii of F\(^-\) and O\(^2-\) are 1.36 Å and 1.40 Å, respectively). Moreover, many oxides have structural analogues among fluorides (for instance, CaO and NaF). Therefore incorporation of fluorine into the structure of high-\(T_c\) cuprates results in formation of **oxyfluorides**, which are structurally similar to the pristine cuprates.

Fluoride anions can replace oxygen anions or/and occupy vacant anion positions in the structure. Thus, it is possible to distinguish two different schemes of cuprates fluorination, described in detail in [72]. According to the first scheme there exists **fluorine incorporation** into the structure of a cuprate. The oxygen content is not changed in this case, but the total number of anions increases because of the additional F\(^-\) anions:

\[
A_mZ_2Q_{n-1}Cu_nO_{m+1+2n-δ} + γ[F] → A_mZ_2Q_{n-1}Cu_nO_{m+1+2n-δ}F_γ
\]  

(10)

Another scheme assumes existence of **anion exchange**, namely substitution of fluorine anions for oxygens. The oxygen content decreases in this case, while the total number of anions remains unchanged:

\[
A_mZ_2Q_{n-1}Cu_nO_{m+1+2n-δ} + γ[F] → A_mZ_2Q_{n-1}Cu_nO_{m+1+2n-δ}F_γ + γ[O]
\]  

(11)

In principle, it is possible to select experimental conditions (temperature and duration of synthesis, fluorination method etc.) favorable for either fluorine incorporation or anion exchange, but in practice both of these processes are usually proceed at the same time.

**1.4.3.1. Synthesis of oxyfluorides**

Different techniques are used for **fluorination** of high-\(T_c\) cuprates. These methods can be distinguished from each other according to occurring reaction mechanism. The most frequently used techniques are based on **solid–state reactions** and **solid–gas reactions**. In both cases
fluorination is carried out by reaction between a precursor (or oxide mixture) and a *fluorinating agent* (a compound containing fluorine atoms).

The method based on solid-state synthesis uses of different fluorides, $MF$ (where $M = \text{Ag}$), $MF_2$ (where $M = \text{Ba, Ca, Cu, Zn etc.}$) or $MF_3$ (where $M = \text{Y etc.}$), as fluorinating agents. Simple oxyfluorides with the common formula $MOF$ (where $M = \text{Y, Eu etc.}$) may also be used for this purpose [73, 74]. Solid-state fluorination is normally a high-temperature synthesis ($> 700^\circ\text{C}$). It has also been shown that cuprate oxyfluorides containing alkaline-earth metals can only be synthesized under high pressure. High-temperature fluorination is not suitable for the synthesis of oxyfluorides, which decompose at high temperatures (for instance, $\text{Sr}_2\text{CuOF}_2$ decomposes above $\approx 460^\circ\text{C}$ [75]).

Low-temperature fluorination could solve some of problems listed above. In this case synthesis is carried out with the use of fluorinating agents typical of the solid–gas synthesis technique, namely $\text{F}_2$ [74, 76], $\text{NH}_4\text{F}$ [77], $\text{NF}_3$ [78], $\text{XeF}_2$ [75, 79, 80] etc., and also with solid–state process reagents, for instance, $MF_2$, where $M = \text{Cu, Ag, Zn etc.}$ Application of $\text{NF}_3$ or gaseous $\text{F}_2$ encounters many problems mainly caused by their high chemical activity. Therefore, mixtures of these substances with inert gas or nitrogen are normally used [74, 76]. One should also note that it is complicated in this case to control the exact quantity of fluorine introduced into the reaction.

Xenon difluoride ($\text{XeF}_2$) is a promising candidate for the synthesis of oxyfluoride superconductors since in fact it combines the advantages of solid–state and solid–gas fluorinating agents. First of all, $\text{XeF}_2$ is solid under normal conditions and can therefore be mixed with a precursor (or added to an oxide mixture) in any desired ratio. Secondly, $\text{XeF}_2$ is not as chemically aggressive as, for instance gaseous $\text{F}_2$. Moreover, during heating it decomposes into $\text{F}_2$ and inert $\text{Xe}$, which decreases the gaseous fluorine activity, and $\text{Xe}$ does not react with any other substance in the system due to its chemical inertness. Fluorination with the use of $\text{XeF}_2$ may result in fluorine incorporation or anion exchange, depending on synthesis temperature. For instance, fluorination of Y-123 [81] leads to fluorine incorporation at low temperatures, whereas with increasing temperature a concurring anion exchange process appears.

Use of highly reactive fluorinating agents brings another serious problem related to the proper choice of material for the synthesis container. Metallic nickel seems to be the material most resistant to the influence of fluorine-containing compounds at temperatures above 300$^\circ\text{C}$. Metallic $\text{Ag}$ and $\text{Au}$ are quite stable as well, but more expensive. Metallic copper is less inert. Thus synthesis in Ni containers is the most preferable. In practice, Ni crucibles placed in copper tubes or bombs with Teflon or nickel gaskets are used. It must be mentioned that fluorination should be preferably carried out in a closed volume to avoid the influence of atmospheric moisture. A closed volume also retains volatile fluorinating agents in contact with the reaction mixture.
I.4.3.2. Oxyfluorides of Hg-based cuprates

A number of investigations have been devoted to synthesis and studies of Hg-based cuprate oxyfluorides [74, 79, 80, 82]. Lattice parameters and $T_c$ values of obtained oxyfluorides are summarized in Table 7.

The presented data show that fluorine incorporation always results in structural changes similar to those observed after oxygenation, namely lattice parameter decrease. It was shown that in Hg-1201 the fluorine anions occupy the extra oxygen positions in the (HgO$_6$) layer, and their amount, $\delta_F = 0.24(2)$ [79, 80] is twice as high as $\delta_O^\gamma = 0.124(9)$, obtained after oxidation of similar samples [25]. This fact is in a good agreement with the ionic doping model.

<table>
<thead>
<tr>
<th>phase</th>
<th>fluorinating agent</th>
<th>lattice parameters</th>
<th>$T_c$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td></td>
</tr>
<tr>
<td>Hg-1201(F)</td>
<td>F$_2$ (N$_2$)</td>
<td>3.862(1)</td>
<td>9.472(3)</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>XeF$_2$</td>
<td>3.8825(3)</td>
<td>9.510(1)</td>
<td>97</td>
</tr>
<tr>
<td>Hg-1212(F)</td>
<td>CuF$_2$ (AgF$_2$)</td>
<td>3.847(1)</td>
<td>12.604(2)</td>
<td>128</td>
</tr>
<tr>
<td>Hg-1223(F)</td>
<td>BaF$_2$</td>
<td>$\approx$ 3.85</td>
<td>$\approx$ 15.85</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>CuF$_2$ (AgF$_2$)</td>
<td>3.848(1)</td>
<td>15.792(6)</td>
<td>135</td>
</tr>
</tbody>
</table>

Table 7.

Results of Hg-based cuprate fluorination.
CHAPTER 5. “STRUCTURE–SUPERCONDUCTING PROPERTIES” RELATIONSHIP OF Hg-BASED CUPRATES

I.5.1. $H_{irr}$ and irreversibility line definitions

Hg-based cuprates, as well as other high-$T_c$ cuprate superconductors, undergo a transition from the superconducting into the normal state over a range of magnetic field values ($H$): i.e. the magnetic field starts to penetrate the superconductor at some value of $H_{c1}$ (also called the lower or the first critical field), while the superconductivity is totally lost at $H = H_{c2}$ (the higher or the second critical field). Between these two $H$ values the sample is partially superconducting and this state is usually denoted as mixed state (Figure 8).

Another particular value of $H$, called irreversibility field ($H_{irr}$), can be distinguished in the $H_{c1}–H_{c2}$ interval. The term “irreversibility” is related to the hysteretic behavior of magnetization ($M$) in an applied magnetic field. A typical $M(H)$ dependence for superconductors is schematically represented in Figure 9a. It has been established that the hysteresis loop width ($\Delta M$) is proportional to the critical current density ($J_c$). For instance, according to a model proposed by Bean [83]:

$$J_c = k \times \Delta M / d$$  \hspace{1cm} (12)

where $d$ is an average sample thickness perpendicular to direction of the applied magnetic field, and $k$ is a constant related to sample shape\(^1\). Increasing the magnetic field results in $\Delta M$ decrease (see Figure 9b), and finally at $H = H_{irr}$ $\Delta M \rightarrow 0$ and therefore $J_c \rightarrow 0$. It is obvious that the $H_{irr}$ value must be considered to be one of the crucial parameters for superconducting materials, since its value is important for different potential applications. $H_{irr}$ is also often used for characterization and comparison of different high-$T_c$ superconducting cuprates. The existence of an irreversibility field is

\(^1\) for instance, a plate, elongated along the field direction has $k = 20$. 

\[27\]
explained by several theories, for instance, by “melting” of the so-called vortex lattice present in the mixed state between $H_{c1}$ and $H_{irr}$.

The temperature dependence of the irreversibility field $H_{irr}(T)$ is called the irreversibility line (IL) (see Figure 8) and was first described in [84]. This line in fact divides the mixed-state region into an irreversible ($\Delta M > 0$, $J_c > 0$) and a reversible field ($\Delta M = 0$, $J_c = 0$) (see Figures 8, 9 a b). However, a uniform analytical description of IL is not yet common; therefore several models and theoretical expressions are used in the literature for this purpose. A short review of the most relevant models used for the IL interpretation is given in [85]. The theoretical description provided by the theory of Matsushita (see, for instance, [86]) fits well in the whole temperature range between $0.25T_c$ and $T_c$. Matsushita deduced the following analytical expression for the irreversibility field:

$$H_{irr} = \frac{K}{T}^{4/(3 - 2\gamma)} \times \left[1 - \left(\frac{T}{T_c}\right)^2\right]^{2m/(3 - 2\gamma)}$$  \quad (13)

where $K$, $\gamma$ and $m$ are numerical parameters.

I.5.2. Relationship between structural factors and $T_c$

The relations between different structural factors and $T_c$ for Hg-based cuprates have been reported quite well in the literature. Here is the short summary of the correlations found:

1. The $T_c$ value depends on the number of (CuO$_2$) planes in the structure ($n$). This dependence has a parabolic shape and reaches its maximum at $n = 3$ ($T_c = 135$ K).

2. $T_c$ depends on extra oxygen content or doping level ($\delta$). This dependence also has a cupola-shaped behavior (see Figure 4): underdoping, as well as overdoping, results in $T_c$ decrease. It is obvious that the $T_c(\delta)$ dependence has cupola-shaped behavior as well.

The $T_c$ value is also connected with the average copper oxidation state ($\nu_{av \ Cu}$). Cuprate superconductors with holes as charge carriers usually exhibit the maximal $T_c$ in the range of
\(v_{av\,Cu}\) values: +2.15 to +2.20; therefore the \(T_c(v_{av\,Cu})\) dependence also has a parabolic shape. However, it should be mentioned that the latter conclusion is only correct for structures containing one atom with variable oxidation state (e.g. copper in cuprates). The discussed \(T_c(v_{av\,Cu})\) dependence may be more complicated when the structure comprises two or more such atoms (as, for instance, in Y-123).

3. Changes in \(\delta\) and \(a\) parameter are correlated. Increasing \(\delta\) results in decreasing \(a\) parameter. Using this fact, parabolic \(T_c(a)\) dependencies are often presented in the literature and used for \(\delta\) value estimation.

Some correlation can also be found between \(T_c\) and the \(c/a\) value, as shown earlier in the example of substituted Hg-based cuprates: decrease of \(c/a\) results in a \(T_c\) decrease.

**1.5.3. Relationship between structural factors and \(H_{irr}\)**

The influence of different structural factors on \(H_{irr}\) and hence on the irreversibility line position for Hg-based cuprates has been less well studied. It is known that ILs of Hg-based cuprates are located between that of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) (which is characterized by one of the highest IL position among all known high-\(T_c\) cuprates) and the ILs of two-layered Bi- or Tl-based cuprate superconductors [87, 88]. Attempts have been done to enhance the irreversibility field both by crystal structure modifications and microstructure changes. However, it has been shown that microstructure changes have almost no influence on \(H_{irr}\) and ILs positions, despite their severe influence on \(J_c\).

Nevertheless, it was found that \(H_{irr}\) enhancement could be achieved as a result of changes on a structural level: the ILs of substituted Hg-based cuprates are situated higher than those of unsubstituted analogues. This effect was particularly clearly observed for \((\text{Hg,Pb})-1223\) [89, 90], \((\text{Hg,Re})-1212\) [91], \((\text{Hg,Re})-1223\) [92], \((\text{Hg,Bi})-1201\) [64], \((\text{Hg,Bi})-1223\) [93], \((\text{Hg,Cu})-1201\) [60], and \((\text{Hg,Pb})(\text{Ba},\text{Sr})-1223\) [71] compounds.

It has been suggested that structural anisotropy \((c/a)\) is a crucial factor influencing \(H_{irr}\) and IL positions. For instance, structures with low \(c/a\) (e.g. Y-123) exhibit rather high values of \(H_{irr}\), while highly anisotropic structures (e.g. Bi-based superconducting cuprates) have significantly lower values. Chemical compression and corresponding \(c/a\) decrease could also occur during substitution.

Another hypothesis assumes an influence of the doping level on \(H_{irr}\): namely, an increase of charge carrier concentration resulting in \(H_{irr}\) enhancement. This suggestion was proved by experimental results showing higher IL locations for overdoped or optimally doped Hg-1223 samples than for underdoped ones [94].
II. Experimental part

CHAPTER 1.
SYNTHESIS METHODS

II.1.1. Initial reagents

HgO (red modification, 99.9), BaO, CaO and CuO were used as starting reagents for the synthesis of Hg-based cuprates. The following metal oxides were also used for the synthesis of substituted Hg-based cuprates with the nominal composition \((Hg_{1-x}M_x)Ba_2Ca_{n-1}Cu_nO_{2n+2+\delta}\) (\(n = 1, 2\) and 3): Tl₂O₃, PbO, WO₃, MoO₃, V₂O₅ and Nb₂O₅. CaO was first prepared by decomposition of CaCO₃ (Merck, 99.0) at 900°C. CuO was obtained by decomposition of CuCO₃·Cu(OH)₂ (99.9) in air at 500°C. BaO was prepared by decomposition of BaO₂ (BDH Lab., 90.0) in a dynamic vacuum \((P = 10^{-6}\text{ atm})\) at 1020°C. All mixing and grinding operations with air-sensitive reagents and products were performed in an Ar-filled glove box, MBraun Labmaster 100 and MB 120 B-G. The purity of all prepared oxides was checked by X-ray powder diffraction.

II.1.2. Synthesis of Hg-based cuprates

The Hg-1223 samples were synthesized in a two-temperature furnace (see Figure 6 a) with the use of sealed silica tubes according to the technique successfully applied earlier for Hg-1201 and Hg-1223 sample preparation [31, 44]. Mixtures of oxides with the nominal composition \((Hg_{1-x}Cu_x)Ba_2Ca_2Cu_3O_8\) \((0.0 \leq x \leq 0.8)\) were placed in alumina crucibles, which were then put in the low-temperature zone \((T_1)\). In the high-temperature zone \((T_2)\) an excess amount of CoO/Co₃O₄ cobalt oxide mixture was used to control oxygen pressure inside the tube. The value of the oxygen pressure (according to the reaction \(6\text{CoO} + \text{O}_2 \rightleftharpoons 2\text{Co}_3\text{O}_4\)) could be approximately estimated from the equation given in [95]:

\[
\log(pO_2)[\text{atm.}] = -15600 / T [\text{K}] + 12.6
\] (14)

The internal mercury pressure in the tube was varied by changing an excess amount of mercury oxide \((m_{HgO, ex})\) placed together with the initial mixture of oxides. The weight of the oxide mixtures \((\approx 2\text{ g})\), the tube length and diameter, and consequently the free volume of the tubes \((\approx 4.5\text{ ml})\) were held constant. Both zones of the furnace were heated simultaneously at a rate of 2–4°C/min. After completion of the heating procedure, the silica tubes were immediately quenched in water. Identical
compositions were obtained in several syntheses (usually 2–5 times) carried out under the same conditions, thus confirming the reproducibility of the described technique.

Syntheses of compounds with the nominal stoichiometry HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ ($n = 1$ and 2) and (Hg$_{1-x}$M$_x$)Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ ($n = 1$ and 2, $x = 0.1$, 0.2) were also performed in evacuated sealed silica tubes: 1) in a three-temperature furnace at 800°C with oxygen and mercury getters (according to the technique described in detail in [3]); 2) in a one-temperature furnace at 800–900°C. In the latter case, mixtures of initial oxides were pressed into pellets with a diameter $\varnothing = 5.5$ mm and then placed in silica tubes without crucibles (inner tube $\varnothing = 6$ mm, external: $\varnothing = 8$ mm). Length of tubes, size and a number of pellets were held constant in all experiments.

Lithium fluoride (99.0) (used as a flux in a number of experiments) was preliminarily dried at 130°C and then sintered at 650°C for 10 h to eliminate absorbed water. Thus obtained LiF was then added to the reaction mixture.

**II.1.3. Thermal treatment of synthesized compounds**

The obtained Hg-1201 and Hg-1223 samples were then heated and annealed in flowing oxygen at 300°C for 24 h in order to increase their oxygen content (or $\delta$ values).

Hg-1201, Hg-1212 and Hg-1223 samples were also reduced either by annealing in dynamic vacuum at 400°C for 20 h or in sealed silica tubes with the use of a Ti getter ($p$(O$_2$) < 10$^{-20}$ atm) at 300–700°C for 24 h. The tubes with getter and reaction mixture were normally quenched in air after completion of the reduction process.

**II.1.4. Fluorination of Hg-1212 and Hg-1223 samples**

Reduced Hg-1212 and Hg-1223 samples were subjected to fluorination, which was performed with XeF$_2$ (provided by the Laboratory of inorganic synthesis, Institute of Applied Chemical Physics “Kurchatov Institute”, Moscow, Russia). Reduced Hg-1212 and Hg-1223 samples were mixed with XeF$_2$ in different ratios and ground in an agate mortar. The obtained mixtures were placed in Ni crucibles, inserted into Cu tubes ($l \approx 130–180$ mm, $\varnothing = 10$ mm, wall thickness: $\approx 2$ mm), which were then evacuated and sealed. The ampoules were annealed at 200°C for 10–15 h and then quenched. All operations with XeF$_2$ were carried out in N$_2$-filled glove box “1BP1-OS” (desiccants: solid KOH and P$_2$O$_5$) to exclude H$_2$O, CO$_2$ etc.
CHAPTER 2.
INVESTIGATION TECHNIQUES

II.2.1. X-ray powder diffraction analysis (XRD)

X-ray powder diffraction (XRD or XPD) analysis of obtained polycrystalline samples was performed at room temperature: 1) in a high-resolution focusing Guinier camera FR-552 (Enraf Nonius Delft; CuK\(_\alpha1\) radiation; effective camera diameter: 228 mm; monochromator: quartz single crystal, curved according to Johansson; inner standard: Ge (\(a = 5.65074(9)\) Å); 2) in a focusing Guinier–Hägg camera (CuK\(_\alpha1\) radiation; effective camera diameter: 80 mm; monochromator: quartz single crystal; inner standard: Si (SRM 640b, \(a = 5.430940(3)\) Å) and 3) using an image-plate Guinier camera (Huber G670). In the first case, the obtained X-ray patterns were measured in an ISA-2 comparator with an accuracy of ± 0.002 mm; intensities of reflections were estimated visually. Lattice parameters calculations were carried out with the use of a Powder program package. The recorded Guinier–Hägg films were evaluated in an automatic film scanner LS-KEJ20, which allows extracting reflection positions and intensity information. The obtained data were treated with the SCAN3 and SCANPI programs [96].

The XRD analysis of several prepared samples (mainly, oxyfluorides) was performed on a STADI-P diffractometer (CuK\(_\alpha1\) radiation; Ge monochromator, transmission mode). Collected data were used for crystal structure determination and analysis of phase composition.

Phase compositions of obtained samples were analyzed using the ICDD PDF-2 database (51 sets). Quantitative analysis was made by estimation of main-reflection intensities for each phase.

II.2.2. Energy-dispersive X-ray spectrometry (EDX)

Cation analyses were made with the use of a JEOL JSM 820 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) spectrometry system, LINK AN10000. Normally about 20 spot analyses of individual grains were made for every sample (2 points for each different grain). Several SEM images were recorded for each sample in order to investigate sample morphology in detail. Search for possible incorporation of light elements (mainly, fluorine from the LiF flux) into the Hg-1212 structure was done using the JEOL 880 SEM equipped with an Oxford LINK ISIS GEM Series 3.00 elemental analysis system.

II.2.3. Infrared spectroscopy (IR)

Infrared (IR) absorption measurements were performed at the Moscow State Academy of Fine Chemical Technology, Moscow, Russia. The IR spectra of Hg-based cuprates were recorded using a
Specord M80 spectrometer in the 400–1200 cm\(^{-1}\) region. Samples were prepared as pellets with admixture of KBr.

**II.2.4. Extended X-ray absorption fine structure (EXAFS) spectroscopy**

X-ray absorption spectra for EXAFS studies were recorded with the EFAFS equipment of the VEPP-3 beamline station (Siberian Synchrotron Radiation Center (SSRC), Novosibirsk, Russia). The recording was performed in transmission mode. Intensities of the primary \((I_0)\) and transmitted \((I_t)\) photon beams were registered with ionization cameras. Standard EXAFS spectrum treatment was performed using the UWXAFS program package [97]. The curve of normalized EXAFS spectra was multiplied by \(k^3\) after subtracting the background (where \(k\) is a photo-electron wave number). Fourier-transforms (FT) have been calculated in the interval \(k = 2.5–13.5\ \text{Å}^{-1}\).

**II.2.5. X-ray absorption near edge structure (XANES) spectroscopy**

The O K-edge and Cu L\(_{2,3}\)-edge X-ray absorption measurements were performed at the High-Energy Spherical Grating Monochromator (HSGM) beam-line of Synchrotron Radiation Research Center (NSRRC, Hsinchu, Taiwan). The X-ray absorption spectra were recorded in the X-ray fluorescence yield mode, using a microchannel plate (MCP) detector. The MCP detector was oriented parallel to the sample surface. Photons were incident at an angle of 45° to the sample normal. The incident photon flux \((I_0)\) was monitored simultaneously by an Ni mesh located after the exit slit of the monochromator. The X-ray absorption spectra were normalized to \(I_0\). The photon energies were calibrated with an accuracy of 0.1 eV, using the O K-edge absorption peak at 530.1 eV and the Cu L\(_3\) white line at 931.2 eV of a CuO reference. The monochromator resolution was set to \(\approx 0.22\ \text{eV}\) at the O K-edge and \(\approx 0.45\ \text{eV}\) at the Cu L\(_{2,3}\)-edges. The O K-edge absorption spectra were corrected for self-absorption effects and normalized to standard absorption cross sections in the energy range 600–620 eV for the O K-edge [98–100].

**II.2.6. Magnetic measurements**

**AC susceptibility** \((\chi)\) measurements of obtained samples were performed by a magnetic-measurement group (Department of Chemistry, Moscow State University, Moscow, Russia). Experiments were carried out by an induction method in the 12–160 K temperature range at an external field of 1 Oe and a frequency of 27 Hz.

Studies of \(\chi(T)\) dependencies at various values of the applied magnetic field were performed at the Department of Physics, Free University of Berlin, Germany. The superconducting properties were determined by using both AC and DC susceptibility measurements with sample quantities of about 200 mg. The temperature dependence of the real and imaginary parts of the AC susceptibility
was recorded, starting at temperatures well above the transition temperature and in magnetic fields up to 14 T. Frequency and AC field amplitude were fixed at 100 Hz and 0.1 mT, respectively. The temperatures of the out-of-phase peak maxima could be determined to about ±0.5 K.

The temperature dependencies of DC transition curves, ZFC as well as FC, were obtained by means of a SQUID magnetometer in applied fields up to 5 T. The superconducting transition temperatures, $T_c$, and the upper critical fields, $H_{c2}$, were determined by the crossover point of the linear extrapolation of the upper transition curve with the horizontal line of the normally conducting region. The error bars again are ±0.5 K. Finally, the merging points of the ZFC and FC curves were used for irreversibility-line determination. As a criterion, the deviation of these two curves of about $10^{-4}$ from the maximum signal value was applied, which corresponds to a measurement error of ±1 K.
CHAPTER 1.
OPTIMIZATION OF Hg-BASED CUPRATE SYNTHESIS

III.1.1. Optimization of the Hg-1223 phase synthesis

First, the nominal composition HgBa$_2$Ca$_2$Cu$_3$O$_8$ of the oxide mixture corresponding to the stoichiometric Hg-1223 phase was used for optimization of synthesis conditions. Preliminary experiments at 785–800°C required long-time annealing and resulted in formation of Hg-1223 samples with large amounts of different impurity phases. That is why a higher temperature ($T_1 = 900°C$) was chosen for all subsequent syntheses, in order to reduce the influence of kinetic factors. The partial pressures of oxygen and of mercury were varied, and optimum values of $T_2 = 1000°C$, $p(O_2) \approx 2.2$ atm, and $m_{\text{Hg}_2\text{O}} = 0.7$ g were determined.

Then the duration of the synthesis was optimized. A number of experiments were carried out in the range of 2–30 h at $T_1 = 900°C$, $T_2 = 1000°C$ and $m_{\text{Hg}_2\text{O}} = 0.7$ g. The influence of annealing time on the phase composition of the (Hg$_{1-x}$Cu$_x$)Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ ($x = 0.2$) sample is graphically shown in Figure 10. Similar results were also obtained with the other samples studied, including

![Figure 10](image_url)

**Figure 10.** XRD patterns representing the influence of synthesis duration on the phase composition of the (Hg$_{0.8}$Cu$_{0.2}$)Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples.
one of stoichiometric composition $x = 0$. The presented data reveal that even a short synthesis time ($t = 3$ h) yields Hg-1223 as the dominant phase. CaHgO$_2$, BaCuO$_2$, Hg-1212 and CuO are the main impurities, indicating incomplete reaction. Increasing $t$ up to 6 h significantly reduced the quantities of all impurity phases and, finally, an increase of synthesis time up to 10–15 h yielded almost pure Hg-1223. Prolongation of the synthesis time up to $t \approx 30$ h resulted in a decrease of the Hg-1223 yield, while increasing quantities of CaO and BaCuO$_2$ formed. This observation is astonishing, assuming that the reaction is under thermodynamic control after 10 h, but a similar effect was also observed in [44]. Probably, an influence of kinetic factors remains crucial even at $T = 900^\circ$C. A tentative explanation is that Hg-1223 with a certain cation composition is initially formed as a metastable phase. Further annealing of the reacting mixture probably leads to formation of Hg-1223 with higher copper content, which is stable under lower mercury pressure. Thus, a synthesis time about 10–15 h seems to be optimal.

It should be noted that occurrence of amorphous phases in the final mixture may distort the results of mole fraction determination, using XRD. However, there are several arguments for estimating the presence of such phases as negligible, and thus for assuming that their influence is insignificant. Namely, the temperature of performed syntheses was quite high (almost close to the melting point) and synthesis duration was rather long. Both these factors promote crystallization of all phases in the product mixture. Moreover, sharp reflections on XRD patterns confirm a high crystallinity of all obtained phases. Evidently, the presented mole fractions are not precise and absolute values, but nevertheless it is reasonable to consider them as approximate data.

Phase-composition analysis of samples prepared from a nominally stoichiometric HgBa$_2$Ca$_2$Cu$_3$O$_8$ mixture under optimum conditions showed the presence of Hg-1223 (80%), BaCuO$_2$ (10%) and CaO (10%). CaHgO$_2$ (2%) was found together with CaO in a number of samples. Probably, it is formed when the silica tubes are quenched. No XRD reflections of CuO were detected in any samples prepared from nominally stoichiometric oxide compositions. Thus the total cation composition of the impurities is Cu-deficient in comparison with the starting content. This fact may be explained by a probable partial substitution of Hg atoms by Cu atoms in the Hg-1223 structure. Further investigations of this assumption were undertaken as will be presented below.

**III.1.2. (Hg$_{1-x}$Cu$_x$)Ba$_2$Ca$_2$Cu$_3$O$_8+\delta$ solid solutions**

Syntheses based on initial mixtures of (Hg$_{1-x}$Cu$_x$)Ba$_2$Ca$_2$Cu$_3$O$_8$ ($x = 0.2$, 0.5 and 0.8) compositions were performed to prepare Hg-1223 with partial substitution of Hg by Cu. The values of $T_1$, $T_2$ and $t$ were the same as those used with the stoichiometric composition described above ($T_1 = 900^\circ$C, $p(O_2) \approx 2.2$ atm and $t = 10$ h), and only the value of $m_{HgO, \text{ex}}$ was optimized in each series of
experiments. XRD patterns of representative samples with $x = 0.0–0.8$ are shown in Figure 11. It is interesting to note that samples prepared with $x = 0.2$ and 0.5 contained more than 95% Hg-1223, which is higher than in the case of $x = 0$. Another important finding is that no samples with $x < 0.8$ contained CuO (as found by XRD), thus indirectly confirming Cu substitution in Hg-1223.

The prepared samples were annealed in an oxygen flow at 300°C. Results of magnetic measurements show that all samples with $x = 0.0–0.8$ exhibit the same value of $T_c^{\text{max}} = 135$ K, which is close to the values usually obtained for the Hg-1223 superconductor [22, 23, 32, 41]. Some of the oxygenated samples of highest quality were studied by EDX analysis. The resulting cation compositions and lattice parameters are listed in Table 8.

It can be seen that lattice parameters and cation compositions for the samples with $x = 0.0$ are close to those with $x = 0.2$ ($a \approx 3.852$ Å, $c \approx 15.820$ Å). Moreover, the sample with $x = 0.0$ contains a large amount of impurities in comparison with samples prepared from mixtures with $x = 0.2$. Probably, a value of about 20% is the lower limit of mercury replacement by copper under these synthesis conditions. This fact is also confirmed by X-ray and neutron powder diffraction data obtained for the (Hg$_{0.8}$Cu$_{0.2}$)Ba$_2$Ca$_2$Cu$_3$O$_8^{+\delta}$ sample. The values obtained for the Hg and Cu occupancies were 0.824(6) and 0.176(6), respectively, closely coinciding with the nominal starting composition ($x = 0.2$) and agreeing with the cation stoichiometry obtained by EDX analysis.

Figure 11. XRD patterns of annealed (Hg$_{1-x}$Cu$_x$)Ba$_2$Ca$_2$Cu$_3$O$_8$ samples with $x = 0.0$, 0.2, 0.5 and 0.8.
Lattice parameters and cation compositions of (Hg\textsubscript{1-x}Cu\textsubscript{x})Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8} samples.

<table>
<thead>
<tr>
<th>nominal x value</th>
<th>lattice parameters after treatment in oxygen flow at 300°C</th>
<th>cation composition (according to EDX)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>0.0</td>
<td>3.8524(2)</td>
<td>15.825(4)</td>
</tr>
<tr>
<td></td>
<td>3.8522(3)</td>
<td>15.824(2)</td>
</tr>
<tr>
<td>0.2</td>
<td>3.8521(4)</td>
<td>15.819(4)</td>
</tr>
<tr>
<td></td>
<td>3.8519(2)</td>
<td>15.820(3)</td>
</tr>
<tr>
<td>0.5</td>
<td>3.8523(3)</td>
<td>15.801(2)</td>
</tr>
<tr>
<td></td>
<td>3.8521(2)</td>
<td>15.798(3)</td>
</tr>
<tr>
<td>0.8</td>
<td>3.8522(4)</td>
<td>15.799(5)</td>
</tr>
</tbody>
</table>

\(^a\)cation compositions are normalized to \(\Sigma\text{(Hg, Cu)} = 4\) (per formula unit).

For samples with higher copper content (\(x = 0.5, 0.8\)) the \(c\) parameter is significantly lower (\(c \approx 15.805\) Å) than for samples with \(x = 0.0\) and 0.2, while the \(a\) parameters for all samples are close to each other (\(a \approx 3.852\) Å). This shortening of the \(c\) axis with increasing \(x\) may also indicate partial replacement of Hg atoms by Cu, since the apical Cu–O distance is expected to be shorter (\(\approx 1.90\) Å) than the corresponding Hg–O distance (\(\approx 2.00\) Å) at this position.

EDX analysis clearly reveals that, even for a nominally stoichiometric starting composition, the prepared Hg-1223 samples contain an excess of copper (about 15–34% of copper substitution at the mercury position). Moreover, a slight tendency to an increase in the copper content with increasing \(x\) could be observed, although the accuracy of the method does not allow us to establish this unambiguously. To be sure that amorphous phases were not present, an additional TEM study of these samples was carried out and also revealed that all studied samples were well crystallized. No significant gradient in cation content was found in any of the studied crystallites. Selected-area electron diffraction patterns for all analyzed crystallites showed only sharp reflections, and no amorphous grains were detected. EDX experiments performed using the TEM agreed well with the EDX / SEM data presented in Table 8.

Such a degree of Cu substitution for Hg in Hg-1223 is quite high in comparison with results obtained earlier. Particularly, 13% and 16% Cu at the Hg position was found by refinement based on single-crystal data [22, 41]. It is interesting to note that these single crystals were also prepared at rather high temperature but under normal pressure. Syntheses of substituted Hg-1223 phases were attempted at 600–800°C, using Hg\textsubscript{0.75}Ba\textsubscript{2.05}Cu\textsubscript{3.2}O\textsubscript{y} as a starting composition [101]. However, a significant amount of CuO was found in the prepared samples. This suggests that the high synthesis temperature used in the study promotes an expansion of the Hg/Cu homogeneity range. Moreover,
such a substitution is accompanied by a decrease of the equilibrium partial pressure of mercury, which in turn favors the formation of more extensively substituted Hg-1223 phases at high temperature. This suggests that synthesis of stoichiometric Hg-1223 samples at 900°C requires higher partial pressures of mercury, which are quite difficult to achieve in the common encapsulation method.

### III.1.3. Optimization of the Hg-1212 synthesis

Synthesis of Hg-1212 samples was carried out in a one-temperature furnace, from an oxide mixture. It is not possible to control partial mercury and oxygen pressures with this technique; therefore obtaining samples with a high content of superconducting phase required an empirical choice of appropriate synthesis conditions, mainly temperature and time of annealing. It should be mentioned that the length of the tubes (≈ 8 cm) and the weight of initial mixture (≈ 1 g) were held as constant as possible in order to maintain the same free tube volume in all experiments.

First of all, the influence of synthesis time on the final phase composition was studied. A number of experiments were carried out in the range 1–15 h. The influence of annealing time on the final phase composition is clearly shown in Figure 12. The obtained data reveal that a short

![Figure 12](image_url)

**Figure 12.** XRD patterns representing the influence of synthesis duration, temperature and LiF addition on the phase composition of the Hg-1212 samples. Reflections corresponding to the Hg-1212 (♦), Hg-1201 (◇) and BaCuO₂ (○) are marked. Only the 2θ region between 20 and 43° is shown.
synthesis time at rather low temperature \( t = 5 \) h and \( T = 840^\circ C \) yields almost no formation of Hg-1212 phase at all, while prolongation of \( t \) up to 10 h leads to some increase of Hg-1212 content. This fact indicates that the desired reaction of Hg-1212 formation is hindered at low temperatures, for instance kinetically, and therefore longer annealing times are necessary.

An increase of synthesis temperature evidently should help in overcoming kinetic factors and result in increase of the reaction rate. To confirm this, a number of experiments were carried out in the range \( 840^\circ C \) up to \( 880^\circ C \) for 10 h, showing that raising the temperature leads to sample quality improvement (Figures 12, 13). However, it should be noted that increasing \( T \) causes an increase of total gaseous pressure inside the tube. Thus, to avoid tube explosion, no experiments were performed at temperatures exceeding \( 880^\circ C \).

### III.1.4. Synthesis with the use of LiF flux

It was found that even samples obtained at quite high \( T (\approx 880^\circ C) \) and with long annealing times \( (\approx 15 \) h) are characterized by a relatively low Hg-1212 content \( (\approx 70–80\%) \) and a large amount of impurity phases. That is why we tried other ways of synthesis optimization, particularly, to study the effect of fluxes. LiF was chosen as a flux in this work.

*Figure 13.* XRD patterns representing the influence of synthesis temperature on the phase composition of the Hg-1212 samples. Reflections corresponding to the Hg-1212 (●), Hg-1201 (◇) and BaCuO₂ (○) are marked. Only the 2θ region between 20 and 43° is shown.
The Hg-1212 samples obtained in all experiments mentioned above were prepared again, under the same conditions but with an addition of LiF flux. The obtained results prove that similar samples synthesized with and without LiF addition have significantly different phase compositions. It was found that even with a rather short synthesis time (≈ 5 h) and low temperature (≈ 840°C) the use of LiF results in a pronounced increase of Hg-1212 yield (see Figure 12). Increasing the time (up to 10–15 h) and temperature (up to 880°C) yielded samples with high Hg-1212 content (≈ 90%); for instance, one may look at the evolution of the Hg-1212 (1 0 1) and (1 0 2) reflections (♦) located between 24°–27° in comparison with the Hg-1201 (1 0 1) reflection (◊) (see Figure 13).

Then the amount of LiF addition was optimized as well. Several syntheses were performed under the same conditions (t = 5 h, T = 880°C) with LiF added in a range of 0.2–5.0 weight %.

It was found that addition of 0.5 weight % LiF (≈ 14.3 mol. %) yields samples with ≈ 90% Hg-1212 phase (Figure 14). Further increase of flux content normally resulted in more impurities (mostly, Hg-1201 and BaCuO₂), thus lowering the sample quality. It should also be mentioned that notable amounts of F-containing admixture phases (for instance, BaF₂) could be observed only at high concentrations of LiF (> 3 weight %).

Figure 14. XRD patterns representing the influence of added LiF (weight %) on the phase composition of the Hg-1212 samples. Reflections corresponding to the Hg-1212 (♦), Hg-1201 (◊) and BaCuO₂ (O) are marked. Only the 2θ region between 20 and 43° is shown.
Analysis performed by scanning electron microscopy (SEM) revealed that the LiF flux addition induced some morphological changes (*Figure 15*). The presence of LiF promoted growth of elongated well-formed crystallites with a characteristic size of 10–30 µm (*Figure 15 a, b*). The cation composition of such crystallites is close to stoichiometric, according to EDX data: Hg : Ba : Ca : Cu = 1 : 2 : 1 : 2. On the contrary, formation of rather uniform, rounded particles was observed without LiF addition (*Figure 15 c, d*). Similar elongated crystallites were also observed in the synthesis of other Hg-based cuprates, but the observed difference in a surface morphology was not as prominent as for Hg-1212.

The appearance of elongated needle-like crystallites indicates a possible LiF flux action mechanism. LiF particles melt at high temperatures ($T_{\text{melt}} \approx 860^\circ\text{C}$) and form local areas of liquid phase in a solid reaction matrix. These liquid regions may lower diffusion problems, thereby facilitating formation and quick growth of Hg-1212 in the form of elongated crystallites. That is why samples with high Hg-1212 phase content could be synthesized even with rather short times ($t \approx 5$ h) and low temperatures ($T \approx 840–850^\circ\text{C}$).

Using a flux sometimes results in occurrence of side reactions involving either the initial compound or the formed product. This leads to formation of impurity phases or even to modification of the synthesized cuprate structure. With LiF, one might expect possible substitution of Li for Cu, and one should also take into account probable F$^-$ anion incorporation and/or partial replacement of O$^{2-}$ anions. Syntheses from samples with different LiF contents in the initial oxide
mixture ($x_{LiF}$) were carried out in order to clarify the influence of F$^-$ anions. The lattice parameters of these samples did not show any correlation with the LiF amount, and XRD phase analysis did not reveal any notable amount of F-containing admixture phase (e.g., BaF$_2$ or CaF$_2$). EDX analysis indicated that the cation–metal ratios in Hg-1212 remained constant, independent of LiF addition, and close to stoichiometric: HgBa$_2$CaCu$_2$ (average composition Hg$_{0.97(4)}$Ba$_{1.93(3)}$Ca$_{1.06(1)}$Cu$_{2.04(3)}$, from 20 spot analyses).

In order to elucidate more carefully the role of LiF, a number of samples were additionally studied using a JEOL 880 SEM, which is equipped with a windowless detector sensitive to light elements ($Z > 6$). Obtained EDX data revealed the cation compositions of studied crystallites to be close to the stoichiometric HgBa$_2$CaCu$_2$O$_6$ and did not show any noticeable amount of fluorine-containing admixtures. Only traces of such impurities could be detected at the outer parts of some crystallites (Figure 16).

Indirect confirmation that Li cations also have no serious influence on the structure of synthesized cuprates was obtained from the results of magnetic susceptibility measurements (see Figure 17). The lattice parameters of the Hg-1212 phase in both samples are close to each other (“a”: $a = 3.8639(3)$ Å, $c = 12.677(4)$ Å; “b”: $a = 3.8631(2)$ Å, $c = 12.671(4)$ Å). This fact indicates nearly the same doping level (namely, a slightly overdoped state) for both samples. The $\chi(T)$ curves almost coincide with each other, as well as $T_c$ values for both samples: “a”: $T_c = 118$ K and “b”: $T_c = 119$ K. This result clearly shows that there is no substitution of Li$^+$ for Cu$^{2+}$ in the sample obtained with LiF flux.

The results thus obtained show that neither lithium nor fluorine atoms from the flux have any essential influence on Hg-1212 crystal structure. It seems that LiF plays its role only at intermediate

\[Figure 16.\] Search for fluorine admixtures in Hg-1212 sample obtained with LiF flux. Marked points correspond to the following compositions: 1: Hg-1212; 2: 1212 + CuO, 3: CaHgO$_2$; 4: “BaCu$_2$O$_2$”; 5: “Ba-Ca-Cu-O”; 6: “Cu-F-O”; 7: “Hg-F-O”.
stages in the Hg-1212 phase formation. Therefore, LiF additive can be recommended for synthesis of Hg-based cuprates, particularly Hg-1212, in order to get samples with a high content of the desired superconducting phase.

Figure 17. Temperature dependence of AC susceptibility for Hg-1212 samples prepared with LiF (\(\nabla\)) (b) and without flux (\(\bullet\)) (a).
CHAPTER 2.
ANION-SUBSTITUTED Hg-BASED CUPRATES

A possibility of fluorine incorporation from LiF into the structure of Hg-based cuprates, as discussed above, could be realized in principle during a reaction of solid-state fluorination. At the same time, it is known that using XeF₂ as a fluorinating agent may lead to different results in comparison with the ordinary solid-state fluorinating agents. That is why it was interesting to synthesize Hg-1212 and Hg-1223 oxyfluorides using XeF₂.

III.2.1. Hg-1223 oxyfluorides

Lattice parameters and $T_c$ values of different fluorinated, reduced and oxygenated Hg-1223 samples are listed in the Table 9.

<table>
<thead>
<tr>
<th>##</th>
<th>fluorination conditions $(R, m, t_1$ and $t_2)^a$</th>
<th>lattice parameters</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$R = 0.5, m = 0.5$; $t_1 = 5$ h, $t_2 = 10$ h</td>
<td>$a = 3.8566(8)$, $c = 15.840(5)$</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>$R = 1.0, m = 0.5$; $t_1 = 5$ h, $t_2 = 16$ h</td>
<td>$a = 3.8556(4)$, $c = 15.840(3)$</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>$R = 1.0, m = 1.8$; $t_1 = 3$ h, $t_2 = 13$ h</td>
<td>$a = 3.8536(4)$, $c = 15.799(4)$</td>
<td>135</td>
</tr>
<tr>
<td>4</td>
<td>$R = 1.5, m = 2.0$; $t_1 = 4$ h, $t_2 = 15$ h</td>
<td>$a = 3.8514(3)$, $c = 15.771(2)$</td>
<td>137</td>
</tr>
<tr>
<td>5</td>
<td>$R = 2.0, m = 2.1$; $t_1 = 2$ h, $t_2 = 15$ h</td>
<td>$a = 3.8501(2)$, $c = 15.773(3)$</td>
<td>138</td>
</tr>
<tr>
<td>6</td>
<td>$R = 5.0, m = 0.8$; $t_1 = 3$ h, $t_2 = 15$ h</td>
<td>$a = 3.8496(3)$, $c = 15.724(3)$</td>
<td>138</td>
</tr>
<tr>
<td>7</td>
<td>$R = 8.0, m = 0.8$; $t_1 = 0$ h, $t_2 = 10$ h</td>
<td>$a = 3.8495(7)$, $c = 15.719(9)$</td>
<td>138</td>
</tr>
<tr>
<td>8</td>
<td>$R = 5.0, m = 1.0$; $t_1 = 0$ h, $t_2 = 10$ h</td>
<td>$a = 3.8479(2)$, $c = 15.721(2)$</td>
<td>137</td>
</tr>
<tr>
<td>9</td>
<td>$R = 5.0, m = 1.0$; $t_1 = 3$ h, $t_2 = 30$ h</td>
<td>$a = 3.8524(4)$, $c = 15.819(2)$</td>
<td>134</td>
</tr>
</tbody>
</table>

$a$ $R$ is the molar ratio of XeF₂ to Hg-1223, $m$ = weight of the sample, $t_1$ and $t_2$ = ramp and dwell time of annealing, respectively.

Variation of the XeF₂/Hg-1223 molar ratio and treatment yielded samples with different levels of fluorination. It is remarkable that incorporation of fluorine into the Hg-1223 structure is accompanied by the valuable decrease of lattice parameters while $T_c$ increases up to 138 K. The
fluorinated samples are arranged in order of decreasing $a$ parameter, which is sensitive to carrier concentration and reflects different fluorine contents. It should be noted that values of lattice parameters for the samples with the highest $T_c$ (## 5–8) are significantly lower than those for the oxygenated sample (## 9). This fact gives indirect evidence of fluorine incorporation in the Hg-1223 structure. Overdoped oxygenated Hg-1223 phase with closely similar values of lattice parameters (prepared under 40 kbar pressure) had much lower $T_c \approx 125$ K [102].

The most important observation is that some samples after fluorination exhibit $T_c = 138$ K which was not reached by samples annealed in oxygen flow. This fact was carefully investigated. The Hg-1223 sample was preliminarily reduced ($T_c = 100$ K) and then divided into two parts. One of them was fluorinated (sample ## 5) while the other part was treated in an oxygen flow. AC susceptibility measurements on these three samples are presented in Figure 18. The fluorinated sample ($a = 3.8501(2)$ Å and $c = 15.773(3)$ Å) showed onset of the transition at 138 K, while the oxygenated sample exhibited $T_c = 134$ K and had significantly larger lattice parameters: $a = 3.8524(4)$ Å and $c = 15.819(4)$ Å. The observed difference of about 4 K between the two transitions is clearly seen in Figure 18. Moreover, this result was reproduced several times, and $T_c = 138$ K was also found for some other fluorinated samples (e.g. ## 6, 7). One may therefore conclude that fluorine incorporation in the Hg-1223 structure increases $T_c$ by 3–4 K in comparison with oxygen-treated samples.

Figure 18. Temperature dependence of AC susceptibility of Hg-1223 samples: after reduction ($\triangle$), heat treatment in oxygen flow (○) and fluorination ( □ ).
To understand the reason for this phenomenon, the sample (# 8) with the lowest impurity content was further investigated by NPD and XRD methods. The X-ray powder diffraction data were obtained on a STADI P diffractometer (Cu$K_\alpha_1$ radiation, linear PSD). It was found that the investigated sample contained 1% CaO (which was introduced in the refinement) and yielded a few unindexed reflections with a maximal intensity about 1%. The XRD experiment allowed refining the occupancy of the (Hg, Cu) position. It was found that this position is occupied jointly by mercury (82.4(6)%), and copper (17.6(6)%). The obtained occupancy parameters are in good agreement with the starting composition (Hg$_{0.8}$Cu$_{0.2}$)Ba$_2$Ca$_2$Cu$_3$O$_8$. Moreover, the NPD refinement showed a significant occupancy (10%) of the oxygen site at the middle of the edge, which was attributed to partial replacement of Hg by Cu [58].

The neutron powder diffraction pattern was obtained at 7 K with the high-resolution Fourier diffractometer (HRFD) at the IBR-2 pulsed reactor. In our experiment, the resolution of HRFD, $\Delta d/d$ was nearly 0.0015, which allowed obtaining precise structural information. In particular, the errors in the interatomic distances were about 0.002–0.003 Å. The Rietveld refinement was done in the $d_{hkl}$ interval from 0.8 to 2.8 Å assuming the 17.6% substitution of mercury by copper obtained from XRD data. The neutron diffraction pattern, theoretical peak positions and difference curve are shown in Figure 19. It is remarkable that the NPD pattern showed only one impurity phase, CaO.

**Figure 19.** ND pattern of the fluorinated Hg-1223 sample (# 8) measured at $T = 7$ K. Experimental points, calculated profile, and the difference curve are shown. The difference curve is normalized on the mean-square deviation. Tick marks at the bottom indicate the position of Bragg peaks for the Hg-1223 phase and CaO.
with refined mass fraction less than 1%. This allowed obtaining structural parameters with high precision, because incorrect handling of impurity phases in the refinement results in significant systematic errors, especially for the occupancy parameters as shown in [23]. The structural parameters of this refinement are listed in Table 10; calculated values of the main interatomic distances are presented in Table 11.

Table 10.

Structural parameters for the (Hg$_{1-x}$Cu$_x$)Ba$_2$Ca$_2$Cu$_3$O$_8$F$_{2\delta}$ phase, refined from NPD data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.84232(2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>15.67451(15)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>231.4096</td>
</tr>
<tr>
<td>$\delta$ = $n(F(1)) + n(F(2))$</td>
<td>0.37 (2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Occupation</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg (0,0,0)</td>
<td>0.86</td>
<td>0.5</td>
<td>1.28 (3)$^g$</td>
</tr>
<tr>
<td>Cu (0,0,0)</td>
<td>0.14</td>
<td>0.5</td>
<td>1.28 (3)$^g$</td>
</tr>
<tr>
<td>Ba (0.5, 0.5, $z$)</td>
<td>0.1697 (1)</td>
<td>0.42 (2)$^f$</td>
<td></td>
</tr>
<tr>
<td>Ca (0.5, 0.5, $z$)</td>
<td>0.3932 (2)</td>
<td>0.42 (2)$^f$</td>
<td></td>
</tr>
<tr>
<td>Cu(1) (0, 0, 0.5)</td>
<td></td>
<td></td>
<td>0.42 (2)$^f$</td>
</tr>
<tr>
<td>Cu(2) (0, 0, $z$)</td>
<td>0.2973 (1)</td>
<td>0.42 (2)$^f$</td>
<td></td>
</tr>
<tr>
<td>O(1) (0, 0.5, 0.5)</td>
<td></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>O(2) (0, 0.5, $z$)</td>
<td>0.3002 (1)</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>O(3) (0, 0, $z$)</td>
<td>0.1261 (1)</td>
<td>0.69 (4)</td>
<td></td>
</tr>
<tr>
<td>F(1) (0.5, 0.5, 0)</td>
<td>0.27 (1)</td>
<td>0.5$^e$</td>
<td></td>
</tr>
<tr>
<td>F(2) (0, 0.5, 0)</td>
<td>0.10 (1)</td>
<td>0.5$^e$</td>
<td></td>
</tr>
</tbody>
</table>

$\chi^2$ | 3.45 |
R$_p$, % | 8.43 |
R$_w$, % | 4.68 |

$^a$ the unit cell volume, for tetragonal structure $V = a^2 \times c$; $^b$ occupancy; $^c$ coordinate $z$ of the atom; $^d$ isotropic temperature parameter; $^e$ the varied parameters were constrained to be equal; $^f$ the varied parameters were constrained to be equal; $^g$ fixed at 0.5 Å$^2$
Table 11.
Main interatomic distances for fluorinated and oxygenated [23] Hg-1223 samples.

<table>
<thead>
<tr>
<th>bond type</th>
<th>fluorinated Hg-1223</th>
<th>oxygenated Hg-1223</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>room temperature</td>
<td>( T = 7 \text{ K} )</td>
</tr>
<tr>
<td>Hg–O(3)</td>
<td>1.983(2)</td>
<td>1.976(2)</td>
</tr>
<tr>
<td>Cu(1)–O(3)</td>
<td>2.692(2)</td>
<td>2.683(2)</td>
</tr>
<tr>
<td>Ba–F(1)</td>
<td>2.6682</td>
<td>2.660(2)</td>
</tr>
<tr>
<td>Ba–O(2)</td>
<td>2.813(2)</td>
<td>2.813(2)</td>
</tr>
<tr>
<td>Ba–O(3)</td>
<td>2.805(2)</td>
<td>2.802(2)</td>
</tr>
<tr>
<td>Cu(1)–O(1)</td>
<td>1.9237(2)</td>
<td>1.9212</td>
</tr>
<tr>
<td>Cu(1)–Cu(2)</td>
<td>3.187</td>
<td>3.177</td>
</tr>
<tr>
<td>Hg–F(1)</td>
<td>2.7205(3)</td>
<td>2.71960</td>
</tr>
<tr>
<td>Hg–F(2)</td>
<td>1.9237</td>
<td>1.9212</td>
</tr>
<tr>
<td>( \angle \text{Cu(2)–O(2)–Cu(2)} )</td>
<td>178.6(5)</td>
<td>178.6(5)</td>
</tr>
</tbody>
</table>

In general, there is good agreement with the results reported in [23] for oxygenated Hg-1223 samples. Two types of extra-anion positions located in the \((\text{HgO}_6)\) layer were also found: A(1) in the middle of the mesh \((0.5, 0.5, 0)\) and A(2) in the middle of the edge \((0.5, 0, 0)\) with occupancies 27(1) and 10(1)%, respectively. The latter value is close to the Cu concentration at the Hg site and may be attributed to additional bonding between Cu and anions. It is interesting to note that these values as well as positional parameters of atoms were almost insensitive to variation of the Hg/Cu ratio at the Hg position within the 10–30% range.

The same two types of extra anion positions were found for the oxygenated Hg-1223 sample \((T_c = 135 \text{ K})\) and for reduced samples with \(T_c = 95 \text{ K}\) and \(107 \text{ K}\) [23]. It was established that, in the reduced sample, the occupancies of both extra anion positions are equal to 8–10(2)%, while oxygen treatment leads to an increase of oxygen occupancy at the A(1) position up to 18(2)%. This value is significantly lower than that (27(1)%) obtained in the present study for fluorinated samples. A similar significant increase of extra anion concentration was found by NPD for fluorinated Hg-1201 in comparison with oxygenated samples exhibiting closely similar \(T_c\) values [79]. Unfortunately, NPD could not distinguish fluorine and oxygen atoms due to their similar coherent scattering lengths. However, on the basis of different anion distribution between these two sites, one can estimate the average copper valence. The obtained values are in the 2.12–2.18 range of \(v_{av \text{Cu}}\), which is typical for hole-doped cuprate superconductors exhibiting optimal \(T_c\).

Incorporation of fluorine results in structure modifications indicated by changes in lattice parameters. The change of the \(a\) parameter reflects the variation of the extra anion concentration in the structure. The dependencies on \(T_c\) vs. the \(a\) parameter for oxygenated and fluorinated Hg-1223
samples are shown in Figure 20. The values of lattice parameters determined by XRD with internal standard were used to avoid possible systematic discrepancies between the data obtained by different techniques. The right part (underdoped range) of the $T_c(a)$ curve for the fluorinated series is close to the oxygenated data down to $a \approx 3.852$ Å and $T_c \approx 134–135$ K. These values correspond to the optimally doped oxygenated Hg-1223 samples. However, further increase of extra anion concentration yields increasing $T_c$ values for the fluorinated series up to 138 K, while oxygenated Hg-1223 exhibits decreasing of $T_c$ due to overdoping. For the fluorinated series the optimal value of the $a$ parameter is smaller than in the oxygenated series, $\approx 3.850$ Å and $\approx 3.852$ Å, respectively. We may therefore conclude that partial replacement of extra oxygen by fluorine in the (HgO$_{\delta}$) layer results in compression of the structure in the $(ab)$ plane, which is accompanied by an increase of the optimal $T_c$ value. This finding differs from the data recently found for Hg-1201, where the $T_c(a)$ dependencies for oxygenated and fluorinated samples almost coincide and have the same values of optimal $T_c = 97$ K and in-plane parameter ($\approx 3.880$ Å) [79].

The dependence of optimal $T_c$ vs. $a$ parameter for the first three members of the Hg-based series and fluorinated Hg-1201 and Hg-1223 is shown in Figure 21. The perfect linear fit is clearly seen with a derivative of $dT_c/da \approx -1.35 \times 10^3$ K/Å. Subsequent compression of the $a$ parameter reflects shortening of the in-plane Cu–O distance because there is no buckling of (CuO$_2$) in Hg-1201 and almost none in the Hg-1212 and Hg-1223 phases. This chemical in-layer compression is accompanied by a significant $T_c$ increase proceeding from Hg-1201 to Hg-1223, as previously reported in [17, 74]. For the latter phase, anion substitution yields a small in-plane compression
\( \Delta a = 0.0023 \text{ Å} \), which is accompanied by a substantial increase (4 K) in \( T_c \). Similar \( T_c \) increase was found for Tl-substituted Hg-1223 with similar change of the \( a \) parameter \( (\Delta a = 0.0024 \text{ Å}) \) [103]. Obtained data show that the origin of this \( T_c \) enhancement cannot be explained by the increase of anion content, as suggested in [103]. It is supported by fluorination of optimally doped Hg-1223. These treated samples did not show \( T_c \) enhancement up to 138 K. It should be noted that the fluorination of highly reduced Hg-1223 could be also a crucial parameter for \( T_c \) enhancement. For instance, less reduced Hg-1223 samples with \( T_c \approx 115 \text{ K} \) reached only \( T_c \approx 135 \text{ K} \) after fluorination [74]. Shortening of the apical Cu–O distance cannot be responsible for the \( T_c \) enhancement, as revealed by the study of Hg-1201 [79].

Taking into consideration all data shown in Figure 21, it is possible to conclude that the origin of this phenomenon is a compressive strain of the (CuO\(_2\)) layer produced by chemical modification of the crystal structure. It is interesting to note that the compressive epitaxial strain for the deposited La\(_{1.9}\)Sr\(_{0.1}\)CuO\(_4\) single-crystal thin film resulted in doubling of \( T_c \) from 25 to 49 K, with a derivative of \( dT_c/da \approx -1.03 \times 10^3 \text{ K/Å} \), which is close to the obtained value [104]. These derivatives are much larger than those produced by an application of external pressure. From crystallographic data published in [21] and the value of \( dT_c/dP \approx 1.7 \text{ K/GPa}^2 \) one can estimate the \( dT_c/da \) derivative for Hg-1223 as equal to \(-1.63 \times 10^2 \text{ K/Å} \), which is about an order of magnitude less than the chemical modification effect.

To understand the origin of this difference one should compare results of structure modification caused by chemical and external pressure. In the first case, that there is no significant

---

**Figure 21.** The dependence on optimal \( T_c \) vs. \( a \) parameter for Hg-based superconducting cuprates.
change in structural arrangement of (CuO₂) layers in the series from Hg-1201 to fluorinated Hg-1223. These layers are flat (Hg-1201) or nearly flat in other phases. Fluorination or Tl-substitution do not significantly change the Cu(2)–O(2)–Cu(2) angle, which is close to 180°: 178.4(4)° for oxygenated Hg-1223 [23], 177.3(1)° for fluorinated Hg-1223 and 178.3(4)° for Tl-substituted Hg-1223 [103]. External pressure changes the arrangement of (CuO₂) layers much stronger, which is reflected in the larger compression of the apical Cu–O distance and the concomitant buckling of these layers. For instance, the Cu(2)–O(2)–Cu(2) angle becomes much smaller (175.0(5)°) in the Hg-1223 structure under 2 GPa pressure, which promotes \( T_c \) enhancement, but with much larger compression of the in-plane bond distances [21]. This buckling angle is an important parameter influencing the superconducting properties of layered cuprates, and the materials with the highest \( T_c \) have less buckled (CuO₂) layers and therefore longer apical distances in the asymmetrical (CuO₅) pyramids [23]. Finally, it is possible to conclude that chemical modification of the structure, causing in-plane compression without change of buckling angle, is a much more efficient factor in enhancing \( T_c \) in layered cuprates than isotropic external pressure, as shown for fluorinated Hg-1223.

**III.2.2. Hg-1223 oxyfluorides under high-pressure**

As mentioned above, application of high external pressure results in significant \( T_c, \text{max} \) increase for Hg-base cuprates (e.g. for Hg-1223 \( T_c, \text{max} \approx 164 \) K at \( P = 31 \) GPa [57]). That is why previously synthesized oxyfluorides with record-high \( T_c \) values were also studied under high pressure.

Measurements of resistance as a function of temperature were performed on samples with different fluorine contents, labeled #1 and #2 in Table 12, following a conventional 4 terminal DC technique and applying pressures in the range of \( P = 4.2–30 \) GPa by using sintered diamond anvils in a Bridgman setup.

<table>
<thead>
<tr>
<th>sample</th>
<th>Hg-1223 : XeF₂ molar ratio</th>
<th>lattice parameters</th>
<th>( T_c ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( a ) (Å)</td>
<td>( c ) (Å)</td>
</tr>
<tr>
<td>#1</td>
<td>1 : 8</td>
<td>3.8496(3)</td>
<td>15.724(3)</td>
</tr>
<tr>
<td>#2</td>
<td>1 : 1</td>
<td>3.8536(4)</td>
<td>15.799(4)</td>
</tr>
</tbody>
</table>

Table 12. Fluorination conditions, lattice parameters and \( T_c \) values for studied Hg-1223 oxyfluorides.

The dependence of resistance vs. pressure for sample #1 is shown in Figure 22. Similar results were also obtained for the other sample (#2). Using the temperature derivative of the resistance one can define the *onset critical temperature* (\( T_c, \text{onset} \)), where derivative departs from its normal behavior, and a *midpoint transition temperature* (\( T_c, \text{mid} \)) determined by the peak of the derivative
(displayed in the inset of Figure 22). The former criterion, usually dominated by thermal fluctuations, is the same as used in [57], and corresponds to formation of small superconducting droplets, while the latter is predominantly related to the appearance of bulk superconductivity.

Pressure increases both $T_{c, \text{onset}}$ and $T_{c, \text{mid}}$, following a parabolic law as depicted in Figure 23. It was found that $dT_c/dP \approx 1.5 \text{ K/GPa}$ for the studied oxyfluorides, which is essentially the same value established for non-fluorinated Hg-1223 ($dT_c/dP \approx 1.7 \text{ K/GPa}$). It is important to underline that the $T_{c, \text{onset}}$ 

**Figure 22.** Normalized resistance of sample #1 as a function of temperature at different pressures. The inset shows the temperature derivative of the resistance.

**Figure 23.** Pressure dependence on $T_{c, \text{onset}}$ and $T_{c, \text{mid}}$ values. The results of similar measurements for Hg-1223 samples [57, 105] are given for comparison.
and $T_c, \text{mid}$ values obtained are clearly higher than those reported for non-fluorinated Hg-1223 samples [57, 105]. In particular, a $T_c, \text{onset}$ value of 166 K for sample #1 at 23 GPa is the highest ever obtained for superconducting cuprates.

### III.2.3. Hg-1212 oxyfluorides

Samples with high contents of Hg-1212 phase were preliminarily reduced in a dynamic vacuum at 400°C for 20 h. Fluorination of the obtained reduced samples was performed at 200°C for 15–30 h in closed Ni crucibles placed in sealed Cu-tubes, using XeF$_2$ as fluorinating agent.

Variation of the XeF$_2$/Hg-1212 molar ratio and the treatment conditions also yielded samples with different levels of fluorination: incorporation of fluorine into the structure of Hg-1212 is accompanied by a decrease of lattice parameters (Table 13). The $T_c$ values are maximal for the samples obtained from the initial mixture with Hg-1212 : XeF$_2$ = 1 : 0.25, and a further increase in fluorine content leads to a $T_c$ decrease down to 119 K (sample F3). This indicates that sample F3, obtained with the largest proportion of XeF$_2$, was in fact overdoped, while the F1 and F2 samples were in almost optimally doped state.

<table>
<thead>
<tr>
<th>sample</th>
<th>Hg-1212 : XeF$_2$ molar ratio</th>
<th>lattice parameters</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
</tr>
<tr>
<td>R</td>
<td>–</td>
<td>3.871(1)</td>
<td>12.752(3)</td>
</tr>
<tr>
<td>O</td>
<td>–</td>
<td>3.8571(2)</td>
<td>12.692(5)</td>
</tr>
<tr>
<td>F1</td>
<td>1 : 0.25</td>
<td>3.8621(5)</td>
<td>12.719(3)</td>
</tr>
<tr>
<td>F2</td>
<td>1 : 0.5</td>
<td>3.8614(2)</td>
<td>12.6872(8)</td>
</tr>
<tr>
<td>F3</td>
<td>1 : 2</td>
<td>3.8551(3)</td>
<td>12.650(2)</td>
</tr>
</tbody>
</table>

All the presented data on $T_c$ values and lattice parameters for fluorinated (F1), reduced (R) and oxygenated in O$_2$ flow (O) samples can be described with one cupola-shaped $T_c(a)$ curve (see Figure 24). It should be noted that, compared to the results of Hg-1201 [79] and Hg-1223 phases (presented above), the fluorinated Hg-1212 samples have larger $a$ parameter values than optimally doped, oxygenated samples ($\Delta a \approx 0.005$ Å). This origin of this phenomenon is still unclear and requires additional structural study.

It was found that some Hg-1212 samples after fluorination exhibit higher $T_c$ values than those annealed in oxygen flow (see Figures 24, 25). The structural features of the Hg-1212 phase obtained, as well as presence of some amount of Hg-1223 homologue (Figure 25b) could give rise
to this effect, and the observed $T_c$ enhancement phenomenon thus also requires further investigation.

**Figure 24.** $T_c$ vs. $a$ parameter for the fluorinated ($\Diamond$) and oxygenated (O) Hg-1212 samples. Samples obtained in the present work are marked (R, O, F1–F3) (table 13). Other data are taken from the table 2.

**Figure 25.** Temperature dependence of AC susceptibility of fluorinated Hg-1212 sample (F1) (a). The temperature interval corresponding to the beginning of superconducting transition is shown as well (b).
CHAPTER 3.
CATION-SUBSTITUTED Hg-BASED CUPRATES

III.3.1. Irreversibility lines of Hg-1223 superconducting cuprates

Hg-based cuprate superconductors exhibit record-high $T_c$ values, but at the same time have quite low irreversibility fields. This fact significantly detracts from their potential application. At the same time, it is known that substituted analogues of Hg-based cuprates have enhanced $H_{irr}$ values, and this prompted us to synthesize and study these compounds.

Investigation of the influence of different substitutions on $H_{irr}$ and the position of the irreversibility line was carried out for samples of Pb-substituted Hg-1223 \{(Hg,Pb)-1223\} with $T_c \approx 132$ K and Hg-1223 oxyfluoride \{Hg-1223(F)\} with $T_c \approx 134$ K. Investigation of the unsubstituted Hg-1223 phase with $T_c \approx 132$ K was performed for comparison. Lattice parameters, $c/a$ and $T_c$ values of the studied Hg-1223 samples are summarized in Table 14.

Table 14.
Lattice parameters, $c/a$ and $T_c$ values of the studied Hg-1223 samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>lattice parameters</th>
<th>$c/a$</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-1223</td>
<td>$3.8541(1)$ $</td>
<td>$ $15.8043(7)$</td>
<td>4.101</td>
</tr>
<tr>
<td>(Hg,Pb)-1223</td>
<td>$3.8502(3)$ $</td>
<td>$ $15.847(2)$</td>
<td>4.116</td>
</tr>
<tr>
<td>Hg-1223(F)</td>
<td>$3.8536(4)$ $</td>
<td>$ $15.799(4)$</td>
<td>4.099</td>
</tr>
</tbody>
</table>

Figure 26. (a) Real parts (upper figure) and imaginary parts (lower figure) of the AC susceptibility for the F-doped Hg-1223 sample. The numbers give the applied DC field (unit: mT). (b) Temperature dependence of the peak values of the AC susceptibility imaginary parts and the upper critical field. The solid line representing IL was fit to Equation 13.
In all cases IL construction was performed on the basis of the peak position evaluation of the out-of-phase component obtained by AC susceptibility measurements at different external magnetic fields (see Figure 26 a, b). Obtained ILs for all three samples are displayed in Figure 27. T values in this diagram are normalized relative to corresponding $T_c$ values.

It should be noted that, although the differences in IL positions are small a clear shift occurs in the high-temperature region ($0.5 < T/T_c < 1$) for both substituted Hg-1223 samples (Pb-doped Hg-1223 and Hg-1223 oxyfluoride) and the unsubstituted Hg-1223 phase. The most enhanced line position is observed for the fluorinated phase. At the same time, in a low-temperature interval ($T/T_c < 0.5$) the ILs of these compounds almost coincide with each other.

### III.3.2. Irreversibility lines of Hg-1212 superconducting cuprates

HgBa$_2$Ca$_2$O$_{6+δ}$ \{Hg-1212\} and (Hg$_{0.8}$Tl$_{0.2}$)Ba$_2$CaCu$_2$O$_{6+δ}$ \{(Hg,Tl)-1212\} samples were synthesized using a one-zone furnace. Lattice parameters, $c/a$ and $T_c$ values of these samples are summarized in Table 15. The EDX analysis confirmed that their cation compositions are correlated rather well with the initial nominal contents: Hg$_{0.92(6)}$Ba$_{1.93(3)}$Ca$_{1.07(4)}$Cu$_{2.07(8)}$O$_{6+δ}$ and (Hg$_{0.74(7)}$Tl$_{0.20(4)}$)Ba$_{1.95(4)}$Ca$_{1.04(6)}$Cu$_{2.05(6)}$O$_{6+δ}$, respectively.

*Figure 27. Irreversibility lines for three studied Hg-based samples. The curves are fit to Equation 13.*
Table 15. Lattice parameters, $c/a$ and $T_c$ values of the studied Hg-1212 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>lattice parameters</th>
<th>$c/a$</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-1212</td>
<td>$a$ (Å) $c$ (Å)</td>
<td>3.29</td>
<td>121</td>
</tr>
<tr>
<td>(Hg,Tl)-1212</td>
<td>$3.8627(3)$ $12.709(4)$</td>
<td>3.8592(2) $12.670(3)$</td>
<td>3.28</td>
</tr>
</tbody>
</table>

Figure 28 shows some results obtained from AC susceptibility measurements. The real and imaginary parts are plotted for Hg-1212 and (Hg,Tl)-1212 samples taken at zero field and at an applied field of 3 T. It is clearly seen that curves of the Tl-substituted sample are shifted to higher temperatures. Moreover, one can establish that the magnetic field has a larger influence on the unsubstituted sample. For instance, the difference in peak positions in the imaginary part, measured at zero magnetic field, is about 3 K, whereas $\Delta T$ is almost 25 K at $H = 3$ T.

The superconducting properties of 1212 samples were determined by means of both AC and DC susceptibility measurements. In order to compare the AC and DC results, Figure 29 a shows examples of (Hg,Tl)-1212 superconducting transition curves obtained with both methods. At low fields the main peak (MP) in the out-of-phase AC signal occurs at a much lower temperature than the DC merging point (DM). Nevertheless, an extended scale shows the existence of a small AC peak (SP, see Figure 29 b), which corresponds to DM in the ZFC and FC curves. This small AC peak, however, is only detectable in the low-field region near $T_c$. With increasing field, the positions

![Figure 28. Real and imaginary parts of AC susceptibility in zero field (curves at higher temperatures) and in a DC field of 3 T (curves at lower temperatures) for Hg-1212 and (Hg,Tl)-1212 superconductors.](image-url)
of the DC merging point and the main AC peak maximum approach each other (Figures 29 a, c) and finally almost coincide at applied magnetic fields above 1 T.

The resulting phase diagram comprising all data for (Hg,Tl)-1212 and Hg-1212 samples
measured in magnetic fields up to 14 T, is plotted in Figure 30. One may note that the phase diagram of Hg-1212 is very similar to that of the Tl-substituted sample. However, it is clearly seen that the IL of (Hg,Tl)-1212 is shifted to higher temperatures.

The experimental data obtained prove that anion- and cation-substituted Hg-1212 and Hg-1223 compounds exhibit enhanced ILs. To clarify this phenomenon, a comprehensive study of Hg-based cuprates was performed, using Hg-1201 as a model phase.

### III.3.3. Cation-substituted Hg-1201 cuprates

The observed $H_{irr}$ enhancement for substituted compounds, as it was mentioned above, could be explained either by anisotropy or doping factor. Therefore it was interesting to perform complex investigation focused on studying of different cation-substituents influence on superconducting properties. This investigation was performed with the use of substituted Hg-1201 phases where Hg$^{2+}$ are partially replaced by other cations with either different oxygen surround (e.g. Mo and V) (see Figure 7) or different oxidation state (e.g. Mo$^{6+}$ and Tl$^{3+}$). Choice of Hg-1201 was stipulated by presence of only one type of Cu-atoms in its crystal structure. Another reason consisted in possibility of reproducible synthesis of Hg-1201 and (Hg,$M$)-1201 single-phased (or almost single-phased) samples.

Samples with the starting nominal composition $(\text{Hg}_{0.9}M_{0.1})\text{Ba}_2\text{CuO}_4+\delta$ ($M = \text{Pb, Tl, W, Mo, V}$ and Nb) were synthesized by the one-temperature furnace method. Unsubstituted Hg-1201 samples with various oxygen content (denoted “a”, “b”, “c” and “d” below) were obtained in a three-temperature furnace, using the technique described in detail in [3], with subsequent annealing in oxygen flow at 300°C for 24 h (sample “a”), in an evacuated silica tube at 300°C for 48 h (“c”) and in vacuum at 400°C for 20 h (“d”). One as-prepared sample (“b”) was also studied.

Lattice parameters of all mentioned Hg-1201 and (Hg,$M$)-1201 samples, their $c/a$ and $T_c$ values are summarized in Table 16.
Table 16.

Lattice parameters, c/a, δ and $T_c$ values of the studied Hg-1201 samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>lattice parameters</th>
<th>c/a</th>
<th>δ</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-1201 (a)</td>
<td>3.8768(24)</td>
<td>9.521(10)</td>
<td>2.46</td>
<td>0.10(1)</td>
</tr>
<tr>
<td>Hg-1201 (b)</td>
<td>3.8840(43)</td>
<td>9.537(13)</td>
<td>2.46</td>
<td>0.06(1)</td>
</tr>
<tr>
<td>Hg-1201 (c)</td>
<td>3.8898(12)</td>
<td>9.549(5)</td>
<td>2.45</td>
<td>0.02(1)</td>
</tr>
<tr>
<td>Hg-1201 (d)</td>
<td>3.8948(7)</td>
<td>9.544(3)</td>
<td>2.45</td>
<td>0.00(1)</td>
</tr>
<tr>
<td>(Hg,Mo)-1201</td>
<td>3.8720(2)</td>
<td>9.4403(4)</td>
<td>2.438</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(Hg,Nb)-1201</td>
<td>3.8833(2)</td>
<td>9.4416(6)</td>
<td>2.431</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(Hg,V)-1201</td>
<td>3.8869(1)</td>
<td>9.4308(3)</td>
<td>2.426</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(Hg,Tl)-1201</td>
<td>3.8933(6)</td>
<td>9.421(2)</td>
<td>2.420</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(Hg,Pb)-1201</td>
<td>3.8833(3)</td>
<td>9.510(1)</td>
<td>2.449</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(Hg,W)-1201</td>
<td>3.8830(3)</td>
<td>9.496(1)</td>
<td>2.446</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> value was not determined.

### III.3.3.1. Investigation of (Hg, M)-1201 compounds

EDX analysis confirmed that the cation composition of all obtained samples was close to stoichiometric. It should be noted that the structural anisotropy factor (c/a) remains almost unchanged on going from the overdoped Hg-1201 sample (“a”) to the highly underdoped one (“d”), while it decreases in a series of substituted (Hg, M)-1201 compounds: $M = Pb – W – Mo – Nb – V – Tl$, and this decrease corresponds to a change in $T_c$ value: from 90 K for (Hg,Mo)-1201 to 74 K for

![EXAFS Hg L₃ spectra](image)

**Figure 31.** Fourier transforms of EXAFS Hg $L_3$-spectra for (Hg₉₀Pb₀₁)Ba₂CuO₄₊δ and (Hg₉₀W₀₁)Ba₂CuO₄₊δ samples. Solid lines correspond to experimental data. Optimized models are drawn by dashed lines.
the Tl-substituted sample.

It is clearly seen that the EXAFS Hg $L_3$-spectra of the (Hg,Pb)-1201 and (Hg,W)-1201 samples coincide. Analysis of Fourier transforms (FT) of these spectra revealed two main features (see Figure 31): 1) a peak at $\approx 1.99$ Å, corresponding to the closest coordination sphere Hg–O (CN = 2), and 2) two peaks ($\approx 3.89$ Å and $\approx 4.04$ Å), caused by overlapping of contributions from Hg...Hg and Hg...Ba spheres. The main difference between obtained FTs is observed in the 2–3 Å interval. The existence of several peaks in this region could be explained by the appearance of additional oxygen atoms required for the cation-substituent coordination sphere.

A new structural $MO_x^y$ fragment, which is formed as a result of the replacement of Hg by another cation, could be considered as an anion group (see Figure 7). In this case, IR-spectroscopy might be sensitive to different oxygen surroundings of the cation-substituent in these samples. There is enough of reliable experimental data concerning vibration frequencies of different coordination polyhedra for the studied transition elements (Mo, Nb, V), obtained both for discrete formations and in condensed structures. IR spectrum of the initial HgBa$_2$CuO$_{4+\delta}$ phase is characterized by a broad intense absorption band with a complex multiplex structure in the 400–650 cm$^{-1}$ interval and a high noise level in the whole investigated spectrum range (Figure 32). This multiplex structure is caused by the complex Hg-1201 crystal structure; while presence of noise is probably created by scattering of radiation from the conduction band electrons. Nevertheless, the appearance of a band (group of bands) is clearly seen in the high-frequency range of the spectrum,

![Figure 32. IR absorption spectra of HgBa$_2$CuO$_{4+\delta}$ and (Hg$_{0.9}$V$_{0.1}$)Ba$_2$CuO$_{4+\delta}$ samples.](image-url)
when Hg is partially replaced by various transition metal cations (V, Mo and Nb, see Figure 32). This fact may be related to $M$–O bond oscillations in a newly formed structural fragment, i.e. a transition-metal coordination polyhedron. The positions of these band absorption peaks correlate with the following frequencies of different cations: 669 cm\(^{-1}\) (Mo), 713 cm\(^{-1}\) (Nb) and 775 cm\(^{-1}\) (V).

Using the obtained spectral data, it is possible to conclude unambiguously the formation of octahedral coordination for Mo and Nb in the structures of substituted phases, and the V coordination number is sufficiently much lower, so that it is possible to assume a five-coordination oxygen surround for vanadium. Moreover, according to the fact that the band of non-symmetrical bond vibrations does not have a distinct multiplex structure, but only a slight asymmetry of the low-frequency slope, this polyhedron is characterized by rather high symmetry.

Investigation of the charge carrier concentration in the obtained substituted samples was performed by means of XANES O $K$-spectra. X-ray absorption spectra for (Hg,\(M\))-1201 (\(M = \text{Tl, V, Mo}\)) samples and their unsubstituted analogues (samples “\(a\)”–“\(d\)”) with different oxygen content were recorded in the energy range 525 to 555 eV (Figure 33). For all samples, two pre-peaks with maxima at about $\approx 528.3$ eV and $\approx 530$ eV could be distinguished for all studied samples in the pre-edge energy range (up to the absorption edge at $\approx 534$ eV) (see Figures 33, 34).

As in earlier high-energy spectroscopy studies on different high-$T_c$ cuprates [106, 107], the spectral features in the O $K$-absorption edges can be assigned to the nonequivalent O sites in the

\[ \text{Figure 33. The XANES O K-edge spectra of non-substituted Hg-1201 samples (labelled \(a\)--\(d\)) (a) and (Hg}_{0.9\text{M}_{0.1})\text{Ba}_2\text{CuO}_{4+\delta} (M = \text{Mo, V, Tl}) samples (b) in the energy range of 525 to 555 eV. The Zhang-Rice states are marked (ZR) on both figures.} \]
crystallographic unit cell, using the differences in the O 1s binding energies between these sites. The O 1s binding energies were found to be lowest for the O sites within the (CuO$_2$) planes of the pyramidal square-planar arrangements. The apex O sites in the (BaO) layers exhibited 1 eV higher binding energy, whereas the O atoms in the (HgO$_{\delta}$) sheets have the deepest O 1s core level shifted to higher binding energies by about 2.2 eV compared to that of the O sites in the (CuO$_2$) planes. This assignment is in agreement with results obtained by several theoretical calculations as well. In analogy to results from other $p$-doped cuprates, this scheme of O 1s binding energies sequence was also adopted to interpret the present data. The low-energy excitation at about 528.2 eV can be ascribed to doping-induced hole states with mostly O 2$p_{x,y}$ character (so-called Zhang-Rice states, denoted ZR) originating from the O sites within the (CuO$_2$) planes. The structure at 530 eV is more difficult to assign to single components since it is due to a superposition of unoccupied O 2$p$ states originating from the O atoms in (BaO) layers and (HgO$_{\delta}$) layers. For some substituted (Hg,M)-1201 ($M = \text{Tl and V}$) samples, an additional pre-peak could be observed at $\approx 531.5$ eV. Probably, it is possible to assign this spectral feature to the appearance of additional oxygen atoms in the (Hg(M)O$_{\delta}$) layers required for coordination around the cation-substituent $M^{2+}$. At the same time, this peak is almost absent in the spectrum of the (Hg,Mo)-1201 sample; the only indication is a shoulder on the high-energy side of the $\approx 530$ eV peak.

It was shown that the intensity of the low energy pre-peak at $\approx 528.3$ eV directly reflects the

![Figure 34](image)

**Figure 34.** The pre-edge interval (525 to 532.5 eV) in the XANES O K-edge spectra of non-substituted Hg-1201 samples (labelled “a”–“d”) (a) and (Hg$_{0.9}$M$_{0.1}$)Ba$_2$CuO$_{4+\delta}$ ($M = \text{Mo, V, Tl}$) samples (b). Zhang-Rice (ZR) states are marked on both figures.
change in hole concentration of the (CuO$_2$) layer. In order to get a quantitative estimate of this hole concentration, the peak at $\approx 528.3$ eV was fitted with a Gaussian function. It was found that hole concentration in the ZR states increases when going from the most reduced sample (d) to the most oxidized one (a) in the series of unsubstituted Hg-1201 samples (Table 17, Figure 35) and from (Hg$_{0.9}$Tl$_{0.1}$)Ba$_2$CuO$_4+\delta$ to (Hg$_{0.9}$Mo$_{0.1}$)Ba$_2$CuO$_4$ for the (Hg,M)-1201 ($M =$ Tl, V and Mo) compounds (Table 17, Figure 35). It should be noted that the spectral weight unit of the low-energy pre-edge peak in the actual O $K$-edge spectra is not an absolute hole number. Therefore the determination of hole concentration in the Hg-1201 and (Hg,M)-1201 compounds is only possible from a comparison with those from O $K$-edge spectra of some standard compound. Usually, polycrystalline $p$-type La$_{2-x}$Sr$_x$CuO$_4+\delta$ is considered as a paradigm for the hole-doped cuprate superconductors [29, 108, 109]. Assuming that in La$_{2-x}$Sr$_x$CuO$_4+\delta$ the number of doped holes is equivalent to the Sr concentration ($x$), one can obtain the O hole concentration per CuO$_2$ plane per unit cell. It is known that the Sr concentration in the La$_{2-x}$Sr$_x$CuO$_4+\delta$ samples with optimized highest $T_c$ (36 K) is close to 0.15 ($x = 0.15$) i.e. corresponds to the La$_{1.85}$Sr$_{0.15}$CuO$_4+\delta$ composition; therefore the calculated number of holes is equal to 0.15 as well. Since the intensity of the low-energy pre-edge peak in the La$_{1.85}$Sr$_{0.15}$CuO$_4+\delta$ O $K$-edge spectrum is equal 1.127 Mbarn-eV, the value of $\approx 7.51$ Mbarn-eV corresponds to one hole in the (CuO$_2$) layer. Using this approach, the absolute hole concentrations were calculated for all studied compounds. The values thus obtained are summarized in Table 17.

It should be also mentioned that in both series the hole concentration increase is correlated with the $T_c$ change (Table 17, Figure 35).

\[ \text{Figure 35. } T_c \text{ vs. hole content for non-substituted Hg-1201 samples (labelled “a”–“d”) (a) and (Hg$_{0.9}M_{0.1}$)Ba$_2$CuO$_4+\delta$ ($M =$ Mo, V, Tl) samples (b).} \]
Table 17.  
Table: Hole concentration of the studied Hg-1201 samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>$I_{528,3}$</th>
<th>hole concentration</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-1201 ($a$)</td>
<td>0.71878</td>
<td>0.09567</td>
<td>90</td>
</tr>
<tr>
<td>Hg-1201 ($b$)</td>
<td>0.59008</td>
<td>0.07854</td>
<td>75</td>
</tr>
<tr>
<td>Hg-1201 ($c$)</td>
<td>0.50828</td>
<td>0.06765</td>
<td>70</td>
</tr>
<tr>
<td>Hg-1201 ($d$)</td>
<td>0.21131</td>
<td>0.02813</td>
<td>65</td>
</tr>
<tr>
<td>(Hg,Tl)-1201</td>
<td>0.2317</td>
<td>0.03022</td>
<td>74</td>
</tr>
<tr>
<td>(Hg,V)-1201</td>
<td>0.25733</td>
<td>0.03356</td>
<td>82</td>
</tr>
<tr>
<td>(Hg,Mo)-1201</td>
<td>0.36381</td>
<td>0.04745</td>
<td>90</td>
</tr>
<tr>
<td>La$<em>{1.85}$Sr$</em>{0.15}$CuO$_{4+\delta}$</td>
<td>1.127</td>
<td>0.15</td>
<td>36</td>
</tr>
</tbody>
</table>

Quantitative estimation of the hole concentration was also performed by means of Cu $L_{2,3}$-edge X-ray absorption spectra. It was shown that the total hole concentration increases when going from sample “$d$” to “$a$” for the unsubstituted Hg-1201 samples and from (Hg$_{0.9}$Tl$_{0.1}$)Ba$_2$CuO$_4$ to (Hg$_{0.9}$Mo$_{0.1}$)Ba$_2$CuO$_4$ for the series of substituted (Hg,$M$)-1201 ($M$ = Tl, V and Mo) compounds. This result is consistent with the data presented above from O $K$-edge spectra, and the established hole concentration increase is also correlated with $T_c$ change in both series.

It should be noted that the obtained values of hole concentrations for the Hg-1201 samples (“$a$”–“$d$”) and especially for (Hg,$M$)-1201 ($M$ = Tl, V, Mo) seem to be substantially lower, if one assumes the ionic doping model ($p = 2\delta$). This fact can be explained by the presence of amorphous Cu-containing phases. That is why, for these samples, XANES spectroscopy is most useful as a powerful tool of $p$ value estimation.

III.3.3.2. Irreversibility lines of (Hg,$M$)-1201 compounds

Irreversibility lines were studied for the samples of Tl-substituted Hg-1201 (Hg$_{0.9}$Tl$_{0.1}$)Ba$_2$CuO$_{4+\delta}$ ($T_c$, onset = 74 K), Mo-substituted Hg-1201 (Hg$_{0.9}$Mo$_{0.1}$)Ba$_2$CuO$_{4+\delta}$ ($T_c$, onset = 90 K), and also Hg-1201 ($T_c$, onset = 88 K), by performing AC susceptibility measurements at various magnetic fields. It was found that application of an external magnetic field has least influence on (Hg,Mo)-1201. For instance, at 9 T the value of $T_c$, onset $\approx$ 15–18 K for (Hg,Tl)-1201, while for the Mo-substituted Hg-1201, $T_c$, onset $\approx$ 45 K at the same value of $H$.

The resulting phase diagram, comprising ILs for Hg1201 and (Hg,$M$)-1201 ($M$ = Tl, Mo) samples is displayed in Figure 36. $T$ values presented in this diagram are normalized with respect to corresponding $T_c$ values. It is clearly seen that the ILs of both substituted compounds are shifted to higher temperatures, compared to unsubstituted Hg-1201. This effect is most significant for
Mo-substituted Hg-1201, and an IL shift is observed in the whole temperature range. For the Tl-substituted compound, the main difference from unsubstituted Hg-1201 appears only in the $T/T_c < 0.7$ region, while in the high-temperature interval ($0.7 < T/T_c < 1$) the ILs of these compounds almost coincide.

One should definitely emphasize the significant enhancement of Mo-substituted sample IL compared to that of the unsubstituted Hg-1201 analogue and also Tl-substituted Hg-1201. Furthermore, this result is interesting from the point of view that the (Hg,Mo)-1201 compound is more anisotropic than (Hg,Tl)-1201 (see Table 16). This fact casts some doubt on the hypothesis of crucial influence of the anisotropy factor on IL positions of cation-substituted (Hg,M)-1201 cuprates. Analysis of data obtained for substituted Hg-1212 and Hg-1223 samples also did not reveal any direct correlation between $c/a$ and $H_{irr}$ values. For instance, Pb-substituted Hg-1223 has the highest $c/a$ parameter value among all studied Hg-1223 samples (see Table 14), but its IL is located between those of Hg-1223 oxyfluoride and unsubstituted Hg-1223.

At the same time, the IL enhancement for (Hg,Mo)-1201 sample compared to that of (Hg,Tl)-1201 corresponds to the hole concentration increase established by XANES. An increase of doping level for Mo-substituted Hg-1201 can be explained by formation of isolated MoO$_6^{6-}$ fragments in the structure instead of HgO$_2^{2-}$ during substitution of Mo$^{6+}$ for Hg$^{2+}$. This substitution obviously provides additional charge carriers. One may note that, in principle, substitution of Tl$^{3+}$ for Hg$^{2+}$ should also result in a similar increase of charge carrier content. Nevertheless, the obtained data do not show any such increase in $p$. This indicates that, in the case of (Hg,Tl)-1201, these substituted fragments (or defects) are clustered so as to form entire (TIO) layers in the structure.
Thus, it is possible to conclude that change of charge carrier concentration (or doping level) is one of the most crucial factors determining the irreversibility line position for Hg-based superconducting cuprates.
I. 1) The influence of different parameters ($T$, $t$, $p$(Hg), $p$(O$_2$)) on the synthesis of Hg-based cuprates in sealed silica tubes has been studied. It was found that optimal conditions yielded samples containing up to 95% of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (Hg-1223).

2) The formation of solid solutions with the formula (Hg$_{1-x}$Cu$_x$)Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (where $x \leq 0.5$) was established.

3) Synthesis in sealed silica tubes with the use of an LiF flux was developed, yielding samples containing up to 90% of HgBa$_2$CaCu$_2$O$_{6+\delta}$ (Hg-1212).

II. 1) Oxyfluorides on the basis of Hg-1212 and Hg-1223, with different $T_c$ values, were obtained for the first time using XeF$_2$ as a fluorinating agent. It was shown that the $T_c(a)$ dependence for both fluorinated phases exhibits a cupola-shaped character, and enhanced $T_c$ values ($\Delta T \approx 3–4$ K) compared to non-fluorinated, optimally doped analogues were observed. In the case of Hg-1223 it is suggested that a crystal structure modification, resulting in a Cu–O distance decrease without a noticeable Cu–O–Cu angle change, may be the significant factor influencing this $T_c$ increase.

2) Hg-1223 oxyfluoride was for first time studied under high pressure. It was found that this compound exhibits a record-high $T_c$ value ($\approx 166$ K) under $P \approx 23$ GPa.

III. 1) It was established that various substituted Hg-based cuprates exhibit enhanced $H_{irr}(T)$ values compared to their unsubstituted analogues. A comprehensive study of these compounds, for example of Hg-1201, indicated that charge carrier doping level change is a more crucial factor determining the irreversibility line than is structural anisotropy.

2) (Hg$_{0.9}$Mo$_{0.1}$)Ba$_2$CuO$_{4+\delta}$ showed the most enhanced irreversibility line position among all studied (Hg,$M$)-1201 compounds.
This thesis would never have been accomplished without help of my colleagues, friends and relatives and I would like to express my deepest gratitude to all of them.

First of all, I would like to acknowledge my supervisors, Prof. Ingrid Bryntse and Prof. Evgeny V. Antipov for giving me the opportunity to work under their command as a PhD student and also for all the support, guidance and encouragement throughout these years.

I would like to thank Dr. Serge N. Putilin, my Russian co-supervisor, for lots of valuable discussions and enormous help at all stages of this work.

My special thanks should be paid to Dr. Konstantin Lokshin, my first supervisor, who introduced me into the field of Hg-based superconductors and helped so much especially at my first steps in science. I am really in dept for many different things he taught me.

A number of my projects were performed in a close collaboration with different scientific groups, all around the world, and I would like to acknowledge all my colleagues for extremely fruitful and, I hope, mutually beneficial co-operation:

Prof. Dr. Klaus Lüders and Dr. Peter Schilbe from the Free University of Berlin (Germany) for the help with susceptibility measurements and interpretation of obtained data. I also would like to thank you very much for inviting me to work in Berlin several times and caring about me during these periods.

Prof. R.-S. Liu and Dr. C.T. Chen from the Synchrotron Radiation Research Center (NSRRC) (Taiwan) for carrying out all the XANES experiments.

Prof. V.V. Fomichev and Dr. M.G. Zaitseva from the Moscow State Academy of Fine Chemical Technology (Russia) for the help with IR-measurements.

Dr. Yu.L. Slovokhotov and Dr. Ya. Zubavichus from the Institute of Organoelement Compounds, Russian Academy of Sciences (Russia) for the valuable assist with EXAFS data interpretation.

Dr. M. Núñez-Regueiro from C.R.T.B.T., C.N.R.S. (France) for performing high-pressure experiments on oxyfluorides.

I appreciate the significant assistance of all my colleagues from Stockholm University and Moscow State University, especially:

Dr. V.A. Alyoshin, thanks for various help with the synthesis and also for providing me with some samples studied within this work.

Dr. K. Jansson, my gratitude for a lot of assistance with SEM facility.
Dr. P.E. Kazin, thanks for the help with susceptibility measurements and also for valuable comments concerning this thesis.

Special thanks to Dr. Sven Westman, for language revision of articles and this thesis.

Ann-Britt Rönnell, numerous of thanks for help in everyday life at the department, and especially for solving my problems with this thesis procedure!

Also I wish to thank all of the former and present people at the Department of Inorganic, Structural and Physical Chemistry, Stockholm University and the Inorganic Crystal Chemistry Lab., Moscow State University, with whom I have spent so much time during these years for providing very friendly and scientifically productive atmosphere.

A thousand thanks to Javie, Mirva and Abbas. You are all, for sure, the best office-mates I can imagine!

Well, fortunately the work is only covers a part of life :), so I also would like to thank all of my friends from another “half life” :). All of you enriched my days and the wonderful moments we spent together are unforgettable and highly appreciated!!!

Especially I wish to thank my “Moscow-friends”: Vladimir Ponomarev, Peter Shkumatov, Julian Pshirkov, Maks Lobanov, Maks Pshirkov, Bogdan Pavlyuk, Mikhail Zhizhin, Aleksey Shchegov, Aleksander Vorushilov, Oleg Afanasyev… and also my “Swedish” company, namely, Aleksander Baev, Oleg Petrov, Serge Ivanov, Pavel Yushmanov, Andrey Egorov, Sigita Urbonaitė, Elena Sandalova and many, many others...

Without you guys and girls the life would have been extremely monotonous and boring!

I also would like to express my deepest gratitude to my dear family, mama, granny and granddad, for their endless support and understanding.

My warmest thanks go to Elena, always being the light of my life, for encouraging me in the most difficult periods of my life, endless patience and love.

I am also very grateful to the following scientific foundations for financial support during the time of my PhD studies, namely, Russian Foundation for Basic Research (Grant RFBR # 03-03-32917), INTAS (Grant # 99-1136) and Volkswagen Stiftung (Grant I/75849).

And finally, let me thank for everything my favourite and, of course, the best team in the world...

I see it... one day we’ll win this Champions League!!!

ВПЕРЕД, ЛОКО!!!

Dmitriy Pavlov (June 2004)
REFERENCES


11. Putlin S.N., Antipov E.V., Marezio M. “Superconductivity above 120K in HgBa$_2$Ca$_n$Cu$_{n+1}$O$_{2n+1}$”, Physica C (1993) 212, 266–270.


16. Paranthaman M., Chakoumakos B.C. “Crystal chemistry of HgBa$_2$Ca$_n$Cu$_{n+1}$O$_{2n+1}$- phase and HgBa$_2$Ca$_n$Cu$_{n+1}$O$_{2n+1}$- phase”, Journal of Solide State Chemistry (1996) 122, 221–230.

17. Antipov E.V., Loureiro S.M., Chaillout C., Capponi J.J., Bordet P., Tholence J.L., Putlin S.N., Marezio M. “The synthesis and characterization of the HgBa$_2$Ca$_n$Cu$_{n+1}$O$_{2n+1}$- phase and HgBa$_2$Ca$_n$Cu$_{n+1}$O$_{2n+1}$- phase”, Physica C (1993) 215, 1–10.


32. Finger L.W., Hazen R.M., Downs R.T., Meng R.L., Chu C.W. “Crystal chemistry of HgBa$_2$CaCu$_2$O$_{8-\delta}$ and HgBa$_2$Ca$_n$Cu$_{2n+2}$O$_{2n+1}$, single crystal X-ray diffraction results”, Physica C (1994) 226, 216–221.
33. Chmaissem O., Wessels L., Sheng Z.Z. “Synthesis and characterization of HgBa$_2$Ca$_n$Cu$_{2n+2}$O$_{2n+1}$ (n = 1, 2 and 3)”, Physica C (1994) 230, 231–238.


88. Welp U., Crabtree G.W., Wagner J.L., Hinks D.G. “Flux pinning and the irreversibility lines in the HgBa$_2$Ca$_2$Cu$_3$O$_{6-\delta}$ and HgBa$_2$Ca$_2$Cu$_3$O$_{6.5}$ compounds”, *Physica C* (1993) 218, 373–378.


91. Salem A., Jakob G., Adrian H. “Resistivity and irreversibility line of (Hg$_{0.8}$Re$_{0.2}$)Ba$_2$Ca$_3$Cu$_{3-n}$O$_{6-\delta}$ HTS thin films”, *Physica C* (2003) 388–389, 747–748.


93. Pelloquin D., Hardy V., Maignan A. “Synthesis and characterization of single crystals of the superconductors Hg$_{0.8}$Ba$_2$Ca$_2$Cu$_2$O$_{6-n}$ (n = 2, 3)”, *Physical Review B* (1996) 54, 16246–16253.


