

# Chemical Stabilization and High Pressure Synthesis of Ba-free Hg-based Superconductors, $(\text{Hg},\text{M})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ ( $n=1\sim 3$ )

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## Abstract

A homologous series of new Hg-based HTSC compounds,  $(\text{Hg},\text{M})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  with  $n=1$  to 3, have been synthesized. The stabilization of the pure phases have been accomplished by chemical doping of third elements such as  $\text{M}=\text{Cr}$ ,  $\text{Mo}$  and  $\text{Re}$ . While the  $\text{Hg}1201$  ( $n=1$ ) phase was readily obtained in this way, it was necessary to simultaneously dope  $\text{Y}$  into the  $\text{Ca}$  site to stabilize the  $\text{Hg}1212$  ( $n=2$ ) phase. On the other hand, single-phase  $\text{Y}$ -free  $\text{Hg}1212$  ( $n=2$ ) and  $\text{Hg}1223$  ( $n=3$ ) samples were synthesized only under a high pressure of 6 GPa. In sharp contrast to the Ba-containing compounds, all the samples prepared in the present study have been quite stable during the synthesis and no deterioration in air has been observed after the preparation.

## 1. Introduction

Recent successive discoveries of the homologous series of  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n=1,2,3,4$ ) [1-4], have stimulated again the further search of new high- $T_c$  superconductors, as this Hg-based family established the record-high  $T_c$  of 134 K and over 160 K under ambient and high pressures, respectively. However, these materials have been found to be sensitive to carbon dioxide or humidity so that they are chemically rather unstable under ambient air. The present authors speculated that substitution of  $\text{Sr}$  for  $\text{Ba}$  would be effective to chemically stabilize these samples and have successfully synthesized recently a Ba-free Hg-based superconductor,  $(\text{Hg},\text{Cr})\text{Sr}_2\text{CuO}_y$  [5]. While its  $T_c$ , approximately 60 K, was relative lower than that of its Ba-based analogue,  $\text{HgBa}_2\text{CuO}_4$ , this Sr-based compound was found to be quite stable under open air.

As it is well recognized, an increase in the number of  $\text{CuO}_2$  sheets in the unit cell structure of layered cuprates is a promising way to enhance  $T_c$ . After the discovery of the  $(\text{Hg},\text{Cr})\text{Sr}_2\text{CuO}_y$ , we have immediately tried synthesis of similarly Cr-doped  $\text{HgSr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n=2,3$ ). However, this attempt was unsuccessful, resulting in the formation of the  $\text{Hg}1201$  phase plus impurity phases only, without any trace of the intended  $\text{Hg}1212$  or  $\text{Hg}1223$  phase. At the same time, we searched for other metal elements by which the Ba-free  $\text{Hg}1201$ ,  $\text{Hg}1212$  and  $\text{Hg}1223$  structures could be structurally stabilized.

In this paper, we report synthesis and superconducting properties of new barium-free mercury-based superconducting systems,  $\text{HgSr}_2(\text{Ca},\text{Y})_{n-1}\text{Cu}_n\text{O}_y$  ( $n=1,2$ ) by chemical doping of  $\text{Cr}$ ,

Mo, or Re into the Hg (or Cu) sites. We have also adopted a high-pressure synthesis technique, by which Hg1233 ( $n=3$ ) could be successfully obtained as a single phase sample. Values of  $T_C$  of the prepared samples were approximately 60~70 K and 90~100 K for 1201 and 1212 compounds, respectively. On the other hand, our Hg1223 showed only  $T_C \sim 59$  K. We believe that, in terms of the carrier doping, this sample is still in the under-doping state with the preparation conditions we have so far examined.

## 2. Experimental

Samples were synthesized by using the two-step solid state reaction technique. Mo-Sr-(Ca,Y)-Cu-O and Re-Sr-(Ca,Y)-Cu-O precursors were prepared by calcining mixed powders of  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$ ,  $\text{MoO}_3$ ,  $\text{ReO}_3$  and  $\text{Y}_2\text{O}_3$  at  $950^\circ\text{C}$  for 24h in air. The obtained precursors were then mixed together with  $\text{HgO}$  and pressed into pellets of  $10\text{ mm}\phi \times 1\text{ mm}$  in dimension. All these procedures have been followed under an open air. Subsequently, each pellet was sealed in an evacuated quartz ampoule, sintered at  $860\sim 940^\circ\text{C}$  for 10~40h and finally quenched to room temperature. For the high-pressure synthesis, the mixed powder of the precursor and  $\text{HgO}$  was loaded into a gold capsule and reacted at  $1000^\circ\text{C}$  for 30 min under a pressure of 6 GPa using a cubic-anvil type high-pressure apparatus [6].

Crystal structure was analyzed by the standard powder X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation. Superconducting properties were studied via DC susceptibility and resistivity measurements. Susceptibility was measured using a SQUID susceptometer (HOXAN HSM-2000X) under an applied field of 10 Oe. Resistivity measurements were performed by the conventional d.c. four-probe method.

## 3. Results

### 3.1. Hg(Sr)1201 compounds

Powder X-ray diffraction analysis revealed that samples with nominal composition of  $(\text{Hg}_{1-x}\text{Mo}_x)\text{Sr}_2\text{CuO}_y$  with  $x=0.3\sim 0.5$  were almost single phase of Hg1201 structure. A powder X-ray diffraction pattern of the sample with  $x=0.3$  is shown in Fig. 1. Diffraction peak indices with the tetragonal unit cell are also displayed in the figure. Samples with  $x=0.1$  and  $0.2$  contained  $\text{SrHgO}_2$  as an impurity phase as we observed in the case of  $(\text{Hg}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CuO}_y$  [5]. In the samples with  $x \geq 0.7$ ,  $\text{SrCuO}_2$  and  $\text{SrMoO}_4$  phases appeared dominantly and their amounts increased with an increase of  $x$ . Lattice parameters,  $a_0$  and  $c_0$ , of the tetragonal unit cell were calculated to be  $3.80\text{ \AA}$  and  $8.86\text{ \AA}$ , respectively, being almost independent of  $x$ . The  $c_0$  value was a little larger than that of  $(\text{Hg}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CuO}_y$ ,  $c_0=8.64\sim 8.71\text{ \AA}$  ( $0.3 \leq x \leq 0.7$ ) [5].

Diamagnetism due to the superconductivity was observed for the Mo-doped samples in the  $x$

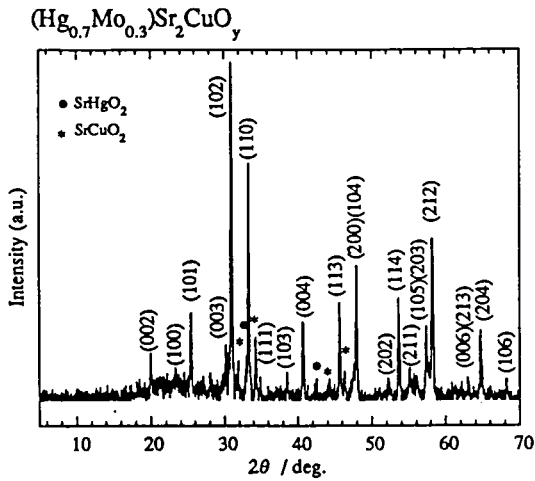


Fig. 1 : Powder X-ray diffraction patterns of  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2\text{CuO}_y$  sample. Diffraction peaks of Hg(Sr)1201 phase are shown with their tetragonal (h, k, l) indices.

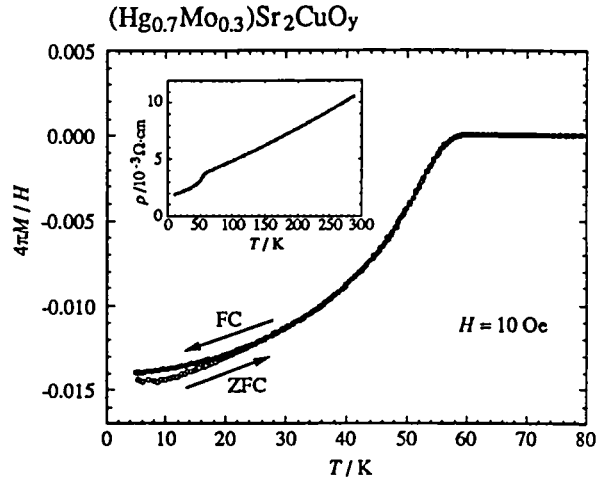


Fig. 2 : Susceptibility and resistivity (inset) curves of  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2\text{CuO}_y$  sample.

range of  $0.1 \leq x \leq 0.7$ .  $T_{C(\text{onset})}$  was found to depend on  $x$  and increased from 52 K for  $x=0.1$  to 72 K for  $x=0.7$ . Figure. 2 shows the zero-field-cooled (ZFC) and field-cooled (FC) susceptibility curves taken under a magnetic field of 10 Oe for  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2\text{CuO}_y$  and the temperature dependence of its resistivity is shown in the inset. The ZFC and FC magnetization curves lie close to each other and the superconducting volume fraction at 5 K estimated from the ZFC curve was 1.5 %. The resistivity curve showed a metallic behavior with a small drop at 58 K corresponding to the  $T_{C(\text{onset})}$  in the magnetic measurement, but the zero resistance was not observed down to 4.2 K. These results and the X-ray diffraction pattern (Fig. 1) indicate that the superconducting coupling between the crystal grains is rather weak in this sample. This behavior is quite different from the  $(\text{Hg}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CuO}_y$  system with  $x=0.3$  which showed the perfect diamagnetism at low temperatures and the zero resistance with a sharp transition at 58 K [5].

The effect of Re substitution for stabilizing the Hg1201 phase was observed at a lower doping level,  $x$ , than Cr or Mo doping. Samples composed of Hg1201 as the major phase were obtained with the  $0.05 \leq x \leq 0.2$  in both samples with nominal compositions,  $(\text{Hg}_{1-x}\text{Re}_x)\text{Sr}_2\text{CuO}_y$  and  $\text{HgSr}_2(\text{Cu}_{1-x}\text{Re}_x)\text{O}_y$ . Figures. 3(a) and (b) show powder X-ray diffraction patterns of  $(\text{Hg}_{0.9}\text{Re}_{0.1})\text{Sr}_2\text{CuO}_y$  and  $\text{HgSr}_2(\text{Cu}_{0.9}\text{Re}_{0.1})\text{O}_y$ . Both patterns are similar to each other only slightly differing in the amount of impurity phases. However, a larger amount of impurity phases such as  $\text{SrHgO}_2$  was compared to the case of the Cr or Mo-substitution. Lattice parameters,  $a_0$  and  $c_0$ , were almost same for the both samples; 3.783 Å and 8.883 Å, respectively.

Superconducting transition was observed with  $x$  up to 0.5 in these sample series.  $T_C$  was approximately 70K independent of  $x$  (0.05~0.2). Figure. 4 shows the ZFC and FC susceptibility curves taken under a magnetic field of 10 Oe for  $\text{HgSr}_2(\text{Cu}_{0.9}\text{Re}_{0.1})\text{O}_y$ , and the resistivity curve is

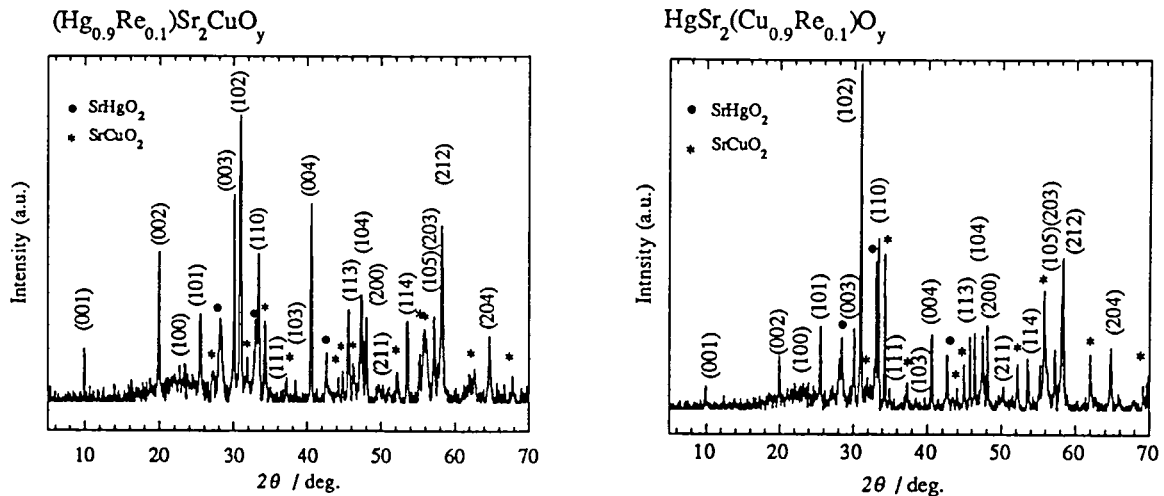


Fig. 3 : Powder X-ray diffraction patterns of  $(\text{Hg}_{0.9}\text{Re}_{0.1})\text{Sr}_2\text{CuO}_y$  (a) and  $\text{HgSr}_2(\text{Cu}_{0.9}\text{Re}_{0.1})\text{O}_y$  (b).

shown in the inset. The superconducting volume fractions at 5 K estimated from the ZFC curve were 1.8% and 9.5% for  $(\text{Hg}_{0.9}\text{Re}_{0.1})\text{Sr}_2\text{CuO}_y$  and  $\text{HgSr}_2(\text{Cu}_{0.9}\text{Re}_{0.1})\text{O}_y$ , respectively. Corresponding to this low superconducting volume fraction, resistivity showed only a small drop at 70 K and did not show zero resistivity down to 4.2 K for the both samples, as was in the case of the Mo-substituted system.

### 3.2 Hg(Sr)1212 compounds

It was found that the simultaneous Y substitution of the Ca site was necessary to stabilize the Cr- or Mo-doped 1212. Figure. 5 shows x ray diffraction patterns of  $(\text{Hg}_{0.7}\text{M}_{0.3})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_y$  for  $x=0\sim 1.0$ . While the Y-free sample ( $x=0$ ) did not contain any trace, the amount of the Hg1212 phase increased with increasing  $x$  up to 0.3 and the samples in the  $x$  range of  $0.3 \leq x \leq 0.7$  were found to be of nearly single phase. Variations of lattice parameters,  $a_0$  and  $c_0$ , with  $x$  are shown in Fig. 6. In the  $x$  range of  $x \leq 0.7$ ,  $a_0$  increases while  $c_0$  decreases with increasing  $x$ .

Samples with  $x=0.1\sim 0.9$  showed superconductivity in the ZFC susceptibility measurements as shown in Fig. 7. The inset shows its blow-up around  $T_c$ . The variation of  $T_c(\text{onset})$ , and superconducting volume fraction at 5 K estimated from the ZFC magnetization with  $x$  are summarized in Fig. 8. The highest  $T_c(\text{onset})$ , 96K, was observed for the sample with  $x=0.3$ , and decreased with increasing  $x$ . Only the sample with  $x=0.3$  exhibited almost the full volume fraction at

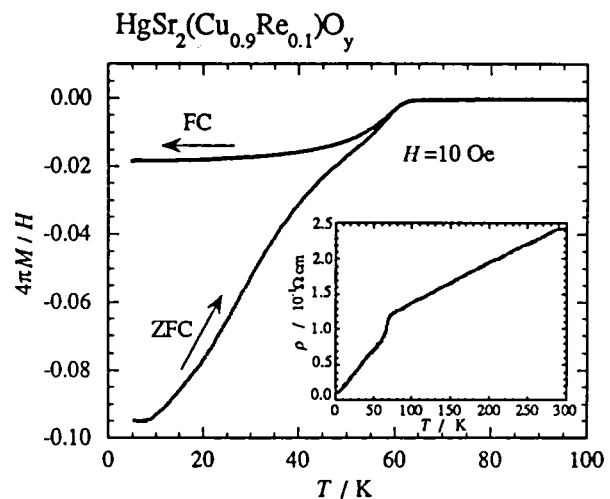


Fig. 4 : Susceptibility and resistivity curves of  $\text{HgSr}_2(\text{Cu}_{0.9}\text{Re}_{0.1})\text{O}_y$ .

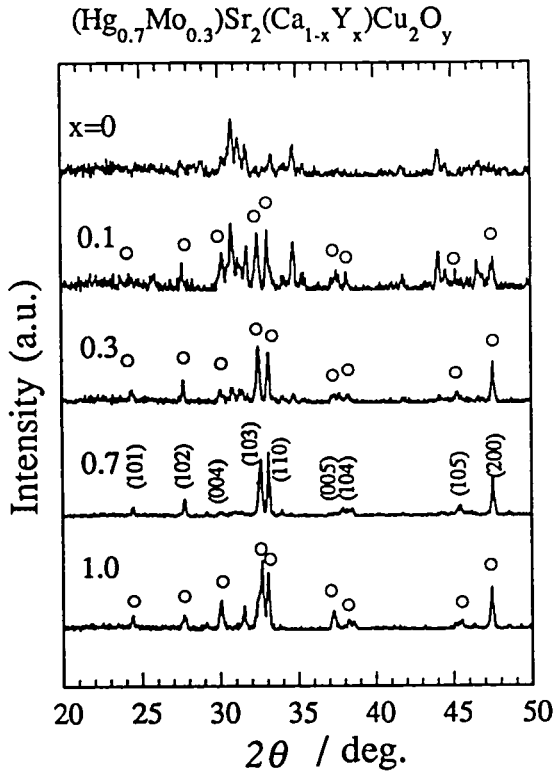


Fig. 5 : Powder X-ray diffraction patterns of  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_y$  as a function of Y content  $x$ . Open circles indicate diffraction peaks of the main phase with the Hg1212 structure.

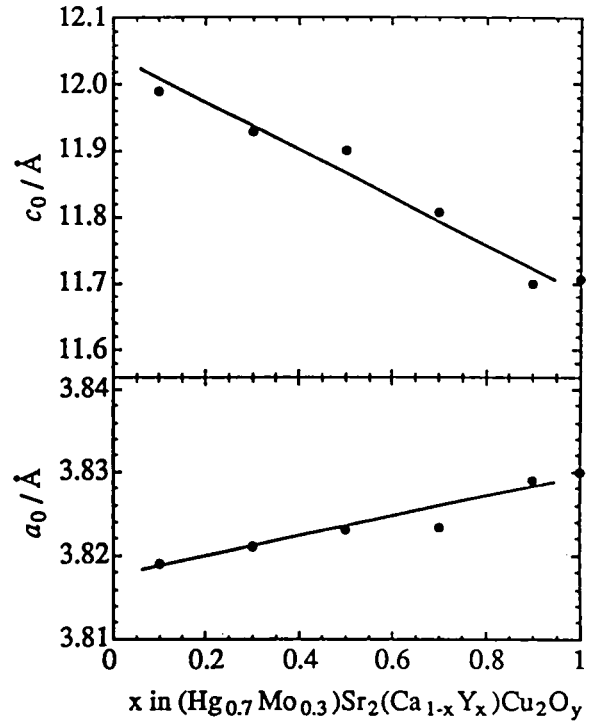


Fig. 6 : Variation in tetragonal lattice parameters of  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_y$  as a function of Y doping.

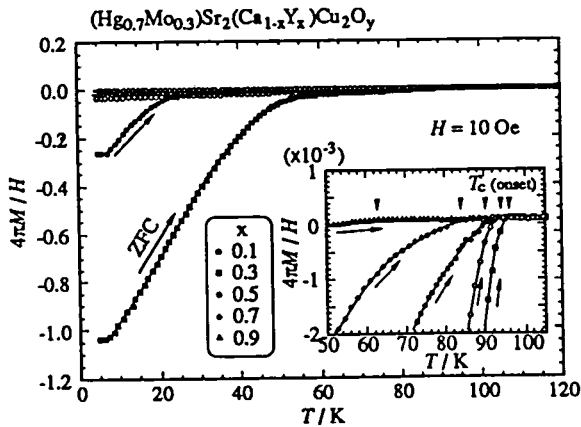


Fig. 7 : ZFC susceptibility curves of  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_y$  taken under  $H=10$  Oe.

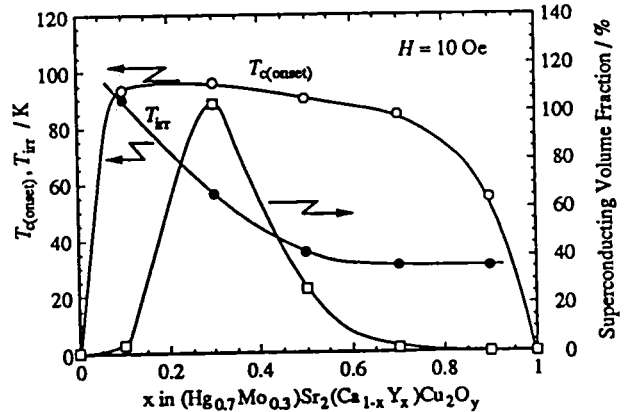


Fig. 8 :  $T_{C(\text{onset})}$ , superconducting volume fraction and irreversible temperature ( $H=10$  Oe) of  $(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_y$ .

5 K, while other samples showed weaker diamagnetism. In the resistivity measurement, this sample with  $x=0.3$  showed  $T_{C(\text{onset})}$  at 95 K and zero resistance at 73 K.

In Fig. 8, we also plot the irreversible temperature,  $T_{\text{irr}}$ , determined from the splitting point

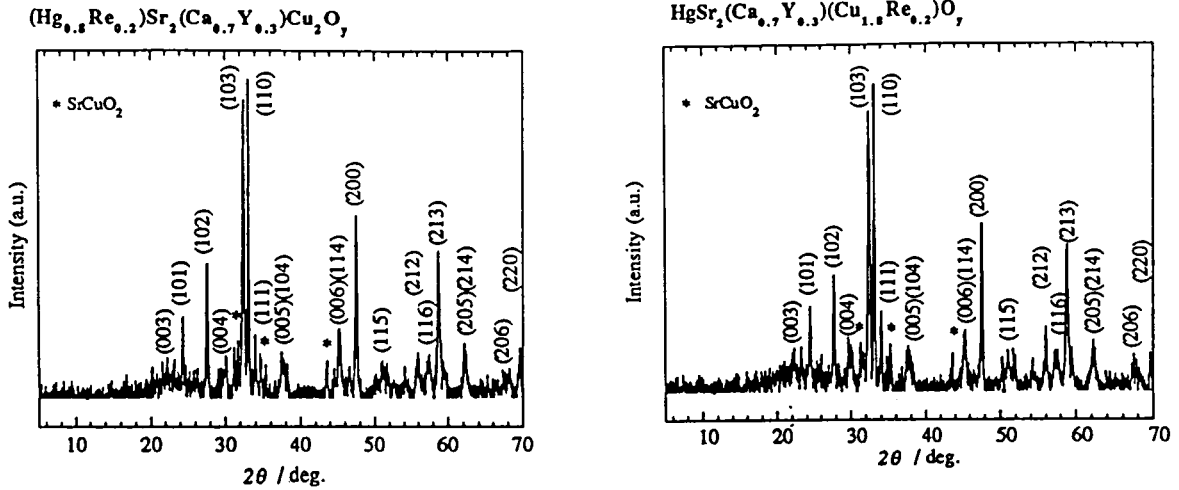


Fig. 9 : Powder X-ray diffraction patterns of Re-doped Hg1212 samples. Hg-site substitution (a) and Cu-site substitution (b).

of ZFC and FC curves taken under the magnetic field of  $H=10$  Oe. It is noteworthy that  $T_{\text{irr}}$  drastically decreases with increasing  $x$ . In the case of the Bi2212 superconductor, it has been recently shown that  $T_{\text{irr}}$  varies strongly as a function of carrier doping, namely,  $T_{\text{irr}}$  is lower as the sample is less hole-carrier doped [7]. By analogy, it is considered that the samples with  $x>0.3$  are in the underdoping state, because the Y substitution for Ca is expected to result in a decrease in the hole carrier concentration. The variations of lattice parameters  $a_0$  and  $c_0$  with  $x$  are quite consistent with this picture.

The simultaneous Re and Y substitutions were also found to be effective to stabilize the Hg1212-structure in both  $(\text{Hg}_{1-x}\text{Re}_x)\text{Sr}_2(\text{Ca}_{1-x'}\text{Y}_{x'})\text{Cu}_2\text{O}_y$  and  $\text{HgSr}_2(\text{Ca}_{1-x'}\text{Y}_{x'})\text{(Cu}_{2-x}\text{Re}_x)\text{O}_y$ . A Y-free sample,  $x'=0$ , was composed of mixed phases of Hg1212, Hg1201 and other impurity phases. On the other hand, samples with  $x=0.2$  and  $x'\geq 0.3$  were obtained as Hg1212 single phase, as shown in Figs. 9(a) and (b). Lattice parameters,  $a_0$  and  $c_0$ , were  $3.818\text{\AA}$  and  $11.879\text{\AA}$ , nearly same in these two samples. Their temperature dependence of resistivity are shown in Fig. 10. Both show  $T_{\text{C}}(\text{onset})$ 's at approximately 100 K and zero resistance at about 83 K. In contrast, the Y-free sample ( $x'=0$ ) did not show zero resistivity down to 4.2 K.

### 3.3 Hg(Sr)1223 compounds

By using the conventional quartz ampoule method, we have tried to synthesize a number of samples with nominal compositions of Hg1223 and 1234 with and without chemical doping. However, we have not been successful to detect any diffraction peaks for these phases. Alternatively, we have recently started high pressure synthesis using a cubic-anvil type apparatus. Figure 11 shows the x-ray diffraction pattern for one of the successfully prepared samples,  $(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ . The calculated lattice parameters were  $a_0=3.859\text{\AA}$  and  $c_0=15.069\text{\AA}$ , clearly exhibiting the formation of almost pure Hg1223 phase. The ZFC susceptibility signal reached over 150% (due to

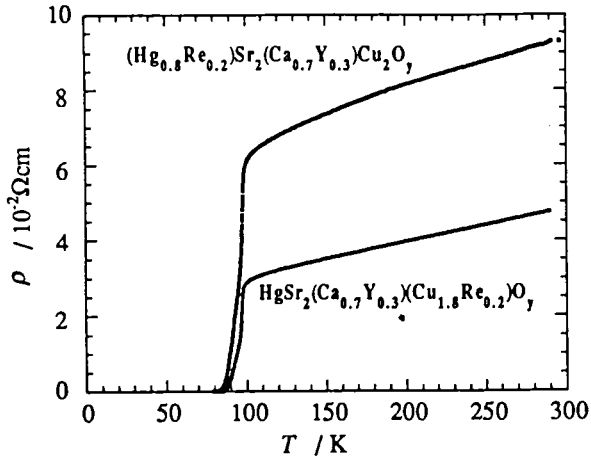


Fig. 10 : Resistivity curves of Re-doped Hg1212 samples.

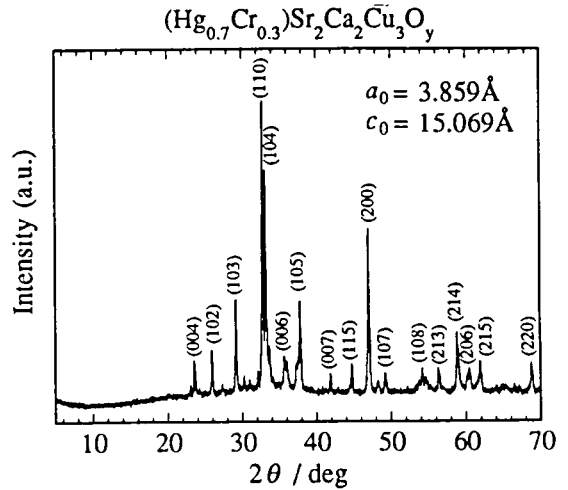


Fig. 11 : X-ray diffraction pattern of high-pressure synthesized  $(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ .

the demagnetization effect). However,  $T_C$  of this sample was only 59 K.

In Fig. 12, the lattice parameters of  $(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  for  $n=1-3$ , are plotted as a function of  $n$ . It must be noted that the 1201 sample was synthesized by the quartz ampoule method, while the 1212 and 1223 samples could be prepared only under high pressure. The increase of  $c_0$ , in unit of  $\sim 3.2 \text{ \AA}$ , corresponds well to the thickness of  $\text{CaCuO}_2$  layer. On the other hand, we have found that  $a_0$  is slightly increasing with  $n$ . This is rather inconsistent with the behavior in the  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  system [1-4] where the decrease of  $a_0$  with  $n$  has been reported. We interpret the tendency in Fig.12 is due to the low carrier doping state of our samples prepared by high pressure technique and this has lead to the observed unexpectedly low  $T_C$  of our 1223 compound.

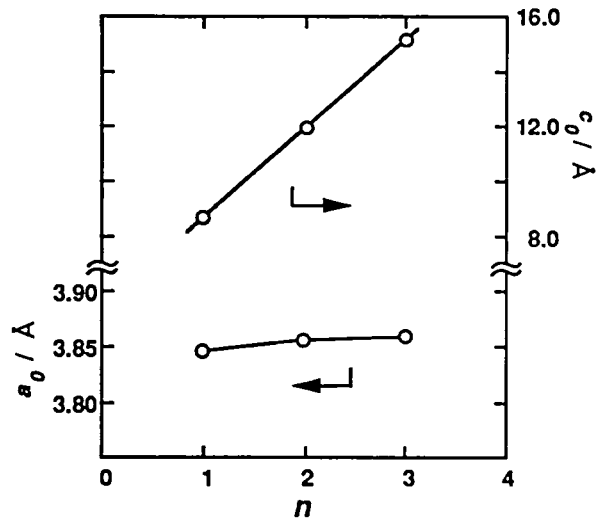


Fig. 12 : Variation of lattice parameters as a function of  $n$  in  $(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ .

#### 4. Discussion

Table 1 summarizes a list of the newly discovered Hg(Sr)-based compounds in the present study, including Hg(Cr)1201 reported in the previous publication [5]. The optimum range of the doping composition,  $x$ , and  $T_C$  should be regarded as approximate values, since we have not

Table 1: List of Ba-free Hg-based superconductors discovered in the present study and in the previous publication [5].

composition	optimal range	$T_C$ /K
$(\text{Hg}_{1-x}\text{Cr}_x)\text{Sr}_2\text{CuO}_y$	$0.3 \leq x \leq 0.4$	~60
$(\text{Hg}_{1-x}\text{Mo}_x)\text{Sr}_2\text{CuO}_y$	$0.1 \leq x \leq 0.7$	~60
$\text{HgSr}_2(\text{Cu}_{1-x}\text{Re}_x)\text{O}_y$	$0.05 \leq x' \leq 1.0$	~70
$(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2(\text{Ca}_{1-x'}\text{Y}_{x'})\text{Cu}_2\text{O}_y$	$0.5 \leq x' \leq 1.0$	n.s.
$(\text{Hg}_{0.7}\text{Mo}_{0.3})\text{Sr}_2(\text{Ca}_{1-x'}\text{Y}_{x'})\text{Cu}_2\text{O}_y$	$0.5 \leq x' \leq 1.0$	~95
$\text{HgSr}_2(\text{Ca}_{1-x'}\text{Y}_{x'}) (\text{Cu}_{1.8}\text{Re}_{0.2})\text{O}_y$	$0.5 \leq x' \leq 1.0$	~100
$(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$	-	~59

attempted the post-annealing effect of these samples under various conditions. In addition, many samples have not shown the zero resistivity and full diamagnetism at the present stage. However, it is evident that, irrespective of the dopant M, the optimized 1201 compounds exhibit  $T_C$  at around 60~70 K and the 1212 compounds show  $T_C$  at 95~100 K. We also believe that  $T_C$  of the 1223 compounds should exceed well over 100 K. These observations support again the universal feature of the layered cuprate superconductors in that the number of the  $\text{CuO}_2$  sheets in the unit cell is the most important parameter in determining the maximum attainable  $T_C$  of a given family of HTSC compounds.

Regarding the site selection of the dopants, it is quite clear from the X-ray analysis that Cr and Mo can be substituted on the Hg site. However, the Re substitution site in both 1201 and 1212 samples is not clear yet. The relatively lower doping composition of Re for effective stabilization of the structure as well as the smaller ionic radius of the Re ion compared to Cr and Mo suggest that the substitution site of Re is the Cu site. Further optimization of the superconducting properties and identification of the doping site and detailed structural analysis using neutron diffraction are under progress.

In summary, we have synthesized 70 K and 100 K-class new Ba-free Hg-based superconductors;  $(\text{Hg},\text{M})\text{Sr}_2\text{CuO}_y$  and  $(\text{Hg},\text{M})\text{Sr}_2(\text{Ca},\text{Y})\text{Cu}_2\text{O}_y$  ( $\text{M}=\text{Cr}, \text{Mo}$  or  $\text{Re}$ ). Cr- and Mo-doping for the Hg site and Y-doping for the Ca site were found to be effective to stabilize the  $\text{Hg}(\text{Sr})1201$  and 1212 crystal structures. We also found that the Re-doping was effective in stabilization at the lower doping level, while the Re substitution site has not been identified. Finally, Cr-stabilized 1223 compound,  $(\text{Hg}_{0.7}\text{Cr}_{0.3})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , has been obtained as a single phase sample by the high-pressure technique, although  $T_C$  (=59 K) of the 1223 phase has not been fully optimized.



## References

- [1] S.N. Putilin, E.V. Antipov, O. Chmaissem and M. Marezio, *Nature (London)* 362 (1993) 226.
- [2] A. Schilling, M. Cantoni, J.D. Guo and H.R. Ott, *Nature (London)* 363 (1993) 56.
- [3] S.N. Putilin, E.V. Antipov and M. Marezio, *Physica C*212 (1993) 266.
- [4] E.V. Antipov, S.M. Loureiro, C. Chaillout, J.J. Caponi, P. Bordet, J.L. Tholence, S.N. Putilin and M. Marezio, *Physica C*215 (1993) 1.
- [5] J. Shimoyama, S. Hahakura, K. Kitazawa, K. Yamafuji and K. Kishio, *Physica C*224 (1994) 1.
- [6] Z. Hiroi, M. Azuma, M. Takano and Y. Takeda, *Physica C*208 (1993) 286.
- [7] K. Kishio, J. Shimoyama, Y. Kotaka and K. Yamafuji, *Proc. 7th Intl. Workshop on Critical Currents in Superconductors*, Alpbach, Austria, Jan 24-27(1994); World Sci. Pub., in press.