Journal of Solid State Chemistry **146,** 151–156 (1999)
Article ID jssc.1999.8321, available online at http://www.idealibrary.com on IDEAL®

Thermogravimetric Study of MHgO$_2$ (M = Ca, Sr, Ba) under Controlled Oxygen and Mercury Partial Pressures and Related Thermodynamics

D. A. Mikhailova, V. A. Alyoshin,[1] and E. V. Antipov

Department of Chemistry, Moscow State University, 119899, Moscow, Russian Federation

and

J. Karpinski

Laboratorium für Festkörperphysik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

Received November 25, 1998; in revised form March 24, 1999; accepted April 8, 1999

A novel method of thermogravimetry under controlled mercury and oxygen partial pressures was developed, which allowed us to obtain the precise thermodynamical data for the equilibrium MHgO$_2$(s) $\Leftrightarrow M$O(s) + Hg(v) + 1/2O$_2$ (M = Ca, Sr, and Ba). Temperature dependencies of equilibrium constants K_p are described by the equations: $\log K_p(\mathrm{CaHgO_2}) = -(9424 \pm 540)/T + (10.28 \pm 0.57)$, (888–1013 K); $\log K_p(\mathrm{SrHgO_2}) = -(10197 \pm 890)/T + (10.10 \pm 0.83)$, (1043–1118 K); $\log K_p(\mathrm{BaHgO_2}) = -(10474 \pm 730)/T + (9.94 \pm 0.64)$, (1098–1163 K). Thermal stability of mercurates increases in the order CaHgO$_2$, SrHgO$_2$, BaHgO$_2$. © 1999 Academic Press

INTRODUCTION

Synthesis of a new family of Hg-based superconductors HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ (1, 2) promoted the intensive study of the phase diagrams and individual compounds existing in the Hg–Ba–Ca–Cu–O system. The alkaline-earth-oxide mercurates MHgO$_2$ (M = Ca, Ba) were found as common impurities in the synthesis of these superconductors. Earlier these compounds, as well as their Sr analogues, were studied by X-ray (3–5) and neutron powder diffraction techniques (3, 5), which showed that they are isostructural and have a delafossite-type structure.

For the synthesis of Hg-based superconductors in a pure form it is necessary to determine their P, T existence conditions taking into account the equilibrium between gaseous and solid components in closed vessels. In this case it is very important to know the formation conditions (including eqilibrium partial pressures of volatile components Hg, HgO, and O$_2$ over solids) for the common Hg-based impurities, namely mercurates MHgO$_2$. By the control of gas pressure inside the reaction vessel it would be possible to suppress the formation of these impurities and to synthesize superconductors in a pure form.

Mercurates decompose under heating according to the reaction:

$$M\mathrm{HgO_2} \Leftrightarrow M\mathrm{O(s)} + \mathrm{Hg(v)} + 1/2\mathrm{O_2}$$

$$K_{p(M\mathrm{HgO_2})} = P(\mathrm{Hg}) \cdot P(\mathrm{O_2})^{1/2}. \qquad [1]$$

The combined thermogravimetry–differential scanning calorimetry (TG-DSC) method has been used before for the investigation of CaHgO$_2$ and BaHgO$_2$ and determination of their thermodynamic properties (6). The following values of the decomposition enthalpy and entropy were determined: $\Delta_r H^\circ_T = 160.0 \pm 8.6$ kJ/mole, $\Delta_r S^\circ_T = 192.1 \pm 9.5$ J/K · mole for CaHgO$_2$ at 830 K and $\Delta_r H^\circ_T = 200.0 \pm 8.0$ kJ/mole, $\Delta_r S^\circ_T = 229.1 \pm 9.1$ J/K · mole at 873 K for BaHgO$_2$.

Sin *et al.* (7) used the thermobaric analyzer (TBA) for the total vapor pressure measurement over a CaHgO$_2$/CaO mixture. The enthalpy and entropy of the reaction Eq. [1] were estimated from the temperature dependence of total vapor pressure in a supposition $P(\mathrm{Hg}) = 2P(\mathrm{O_2})$: $\Delta_r H^\circ_T = 138$ kJ/mole, $\Delta_r S^\circ_T = 157$ J/K · mole at the temperature range of 1100–1200 K.

The TG-DSC technique has several limitations because even if it allows one to determine the decomposition temperature and the reaction heat, the partial pressures and entropy can still be roughly estimated from experimental data. The P(Hg) pressure for such an equilibrium can be directly

---

[1] To whom correspondence should be addressed. Fax: 7-095-939-4788; E-mail: alyoshin@inorg.chem.msu.ru.

0022-4596/99 $30.00

measured and the P(Hg) vs. T or $P(O_2)$ dependencies can be determined by the static weight technique (SWT), which we used previously for the investigation of the equilibrium between $HgBa_2CuO_{4+\delta}$, Ba_2CuO_{3+x} and gas phase (8). The TBA technique allows one to measure the total vapor pressure. However, this method is very sensitive toward vapor contamination by any volatile impurities. Moreover, both techniques (SWT and TBA) require a long time for correct measurements, especially at low temperatures, due to the necessity of achieving an equilibrium between solid and gaseous phases.

In the present work a method similar to the SWT technique was developed for the study of the equilibrium between MHgO$_2$ and gas phase—the method of thermogravimetry under controlled mercury and oxygen partial pressures. This method is a variation of the well-known "mass-transfer method" of partial vapor pressure determination of volatile component over metal alloys, described, for instance, in Ref. (9).

THERMOGRAVIMETRY UNDER CONTROLLED OXYGEN AND MERCURY PARTIAL PRESSURES

The method of thermogravimetry under controlled partial mercury P(Hg) and oxygen $P(O_2)$ pressures was used for the determination of equilibrium P(Hg) and $P(O_2)$ in three phase equilibrium $S(M\mathrm{HgO}_2)S(M\mathrm{O})\mathrm{V}$ of the reaction (Eq. [1]) and related thermodynamics calculation.

The studied samples, consisting of $M\mathrm{O}/M\mathrm{HgO}_2$ two phase mixtures (M = Ca, Sr, Ba), were heated inside a horizontal silica tube, where P(Hg) and $P(O_2)$ partial pressures were fixed. The starting temperature was chosen, taking into account preliminary measurements, to satisfy conditions when $K_{p(M\mathrm{HgO}_2)} < P(\mathrm{Hg}) \cdot P(\mathrm{O}_2)^{1/2}$. Synthesis of MHgO$_2$ according to Eq. [1] takes place. The equilibrium constant of the reaction increases with rising temperature and finally it corresponds to the equilibrium state between gas and solid phases at temperature $T_{\mathrm{eq.}}$, where $K_{p(M\mathrm{HgO}_2)} = P(\mathrm{Hg}) \cdot P(\mathrm{O}_2)^{1/2}$. Further temperature increase results in the decomposition of MHgO$_2$ because $K_{p(M\mathrm{HgO}_2)} > P(\mathrm{Hg}) \cdot P(\mathrm{O}_2)^{1/2}$. The mass changes of the studied sample can be used for the determination of equilibrium parameters.

The P(Hg) and $P(O_2)$ values can be fixed independently inside the vessel. Two techniques have been used to control these pressures.

In the first method $P(O_2)$ was fixed using the equilibrium $Co_3O_4 = 3CoO + 1/2O_2$ at $T^{(3)}$ (Fig. 1a) as described in Ref. (8). Mercury pressure P(Hg) calculated from the reference data (10) was controlled by eqilibrium:

$$\mathrm{HgO(s)} = \mathrm{Hg(v)} + 1/2\mathrm{O}_2; \quad K_{p(\mathrm{HgO(s)})} = P(\mathrm{Hg}) \cdot P(\mathrm{O}_2)^{1/2}.$$

Accordingly, HgO was placed in another part of the silica tube and heated to $T^{(1)}$ at fixed $P(O_2)$.

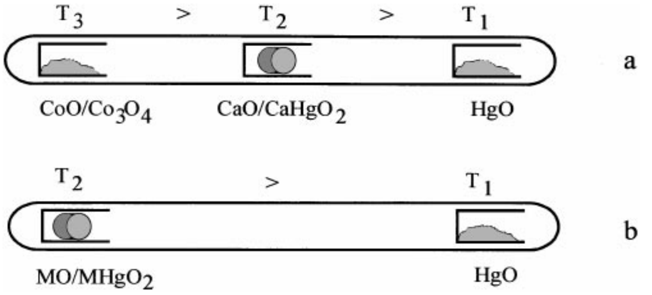

FIG. 1. Schemes of silica ampoules in thermogravimetry under controlled mercury and oxygen partial pressures: (a) a three-temperature variation; (b) a two-temperature variation.

This method was used for the investigation of $CaHgO_2$. The sample was placed in the central part of the evacuated sealed silica tube at the intermediate temperature $T^{(2)}$ (Fig. 1a). We assume that P(Hg) and $P(O_2)$ remain constant within the vessel. This assumption is correct if P(HgO) at $T^{(1)}$ and $T^{(2)}$ are similar and their difference is much smaller than the P(Hg) and $P(O_2)$ values. Calculations based on the recent thermodynamic data from (11) for the gaseous phase equilibrium $\mathrm{HgO(v)} = \mathrm{Hg(v)} + \mathrm{O}_2$ show that P(HgO) values are lying in the range 2–6% of the total vapor pressure for our experimental conditions (P(Hg), $P(O_2)$ and T), thus supporting our assumption.

The second technique, a simplified modification of the first one, allows us to take into account HgO(v) partial pressure and its gradient inside the closed vessel. Similar K_p values were obtained for $CaHgO_2$ by both measurements, and this supports our assumption for the first technique. In the second method, HgO(s) was used only to control mercury and oxygen partial pressures (Fig. 1b). This approach is possible for the investigation of these compounds, because the vapor composition over MHgO$_2$ and HgO has the same stoichiometry $\mathrm{Hg:O_2} = 2:1$ and, consequently, $P(\mathrm{Hg}) = 2P(\mathrm{O}_2)$.

In this case HgO was placed in one side of the evacuated and sealed silica tube at temperature $T^{(1)}$ and the $M\mathrm{HgO}_2/M\mathrm{O}$ mixture in another side at temperature $T^{(2)} > T^{(1)}$. Mercury and oxygen partial pressures and total vapor pressure at $T^{(1)}$ can be calculated from the thermodynamic values (10), taking into consideration the following equilibria.

$$\mathrm{HgO(s)} \Leftrightarrow \mathrm{Hg(v)} + 1/2\mathrm{O}_2; \quad K_{p(\mathrm{HgO(s)})} = P(\mathrm{Hg}) \cdot P(\mathrm{O}_2)^{1/2}$$

$$\mathrm{Hg(v)} + 1/2\mathrm{O}_2 \Leftrightarrow \mathrm{HgO(v)};$$

$$K_{p(\mathrm{HgO(v)})} = P(\mathrm{HgO})/P(\mathrm{Hg}) \cdot P(\mathrm{O}_2)^{1/2},$$

where P(HgO), P(Hg), $P(O_2)$ are equilibria partial pressures over HgO(s), and the total pressure $P^{(1)}_{\mathrm{total}}$ over HgO at $T^{(1)}$ is equal to

$$P_{\text{total}}^{(1)} = P(\text{Hg}) + P(\text{O}_2) + P(\text{HgO}).$$

In another side of the tube at temperature $T^{(2)}$, the following equilibria take place over two-phase mixture of MO and MHgO$_2$:

$$M\text{HgO}_2(\text{s}) \Leftrightarrow M\text{O}(\text{s}) + \text{Hg}(\text{v}) + 1/2\text{O}_2;$$

$$K_{\text{p}(M\text{HgO}_2)} = P(\text{Hg}) \cdot P(\text{O}_2)^{1/2}$$

$$\text{Hg}(\text{v}) + 1/2\text{O}_2 \Leftrightarrow \text{HgO}(\text{v});$$

$$K_{\text{p}(\text{HgO}(\text{v}))}^{(2)} = P(\text{HgO})/P(\text{Hg}) \cdot P(\text{O}_2)^{1/2}$$

where $P(\text{HgO})$, $P(\text{Hg})$, $P(\text{O}_2)$ are equilibria partial pressures over $M\text{HgO}_2$. Total pressure over $M\text{O}/M\text{HgO}_2$ mixture at $T^{(2)}$ is expressed as

$$P_{\text{total}}^{(2)} = P(\text{Hg}) + P(\text{O}_2) + P(\text{HgO}).$$

In these last equations, which describe the equilibria at $T^{(2)}$, $K_{\text{p}(M\text{HgO}_2)}$, $P(\text{Hg})$, $P(\text{O}_2)$, $P(\text{HgO})$, and $P_{\text{total}}^{(2)}$ are parameters to be calculated for the $T_{\text{eq.}}^{(2)}$ temperature when equilibrium total pressure over $M\text{O}/M\text{HgO}_2$ mixture at $T^{(2)}$ is equal to total vapor pressure over HgO at $T^{(1)}$ ($P_{\text{total}}^{(2)} = P_{\text{total}}^{(1)}$).

In order to determine $T_{\text{eq.}}^{(2)}$, a $M\text{O}/M\text{HgO}_2$ mixture should be heated starting from $T^{(2)} < T_{\text{eq.}}^{(2)}$ at constant total vapor pressure $P_{\text{total}}^{(1)}$. When $T^{(2)} < T_{\text{eq.}}^{(2)}$ and, consequently, $P_{\text{total}}^{(2)} < P_{\text{total}}^{(1)}$, mass transfer takes place from HgO to $M\text{O}/M\text{HgO}_2$ leading to formation of $M\text{HgO}_2$, while at higher temperatures, $T^{(2)} > T_{\text{eq.}}^{(2)}$ ($P_{\text{total}}^{(2)} > P_{\text{total}}^{(1)}$), the reverse process takes place with $M\text{HgO}_2$ decomposition and mercury oxide condensation. Only in the case of $T^{(2)} = T_{\text{eq.}}^{(2)}$, when $P_{\text{total}}^{(2)} = P_{\text{total}}^{(1)}$, no mass transfer occurs, and, consequently, $T_{\text{eq.}}^{(2)}$ is determined as a temperature corresponding to the maximum mass of the $M\text{O}/M\text{HgO}_2$ sample heated at constant rate.

This method has certain advantage in comparison with TG-DSC and SWT methods. First, it is not necessary to have an individual $M\text{HgO}_2$ phase as in the TG method. Moreover, in the latter technique it is much more difficult to fix mercury pressure inside the device. In contrast with the SWT method, it is not necessary to reach for the completeness of the reaction with HgO in order to reach an equilibrium state. In our method partial pressures are fixed and we have to detect temperature $T_{\text{eq.}}^{(2)}$ only, when these fixed partial pressures are equal to equilibrium ones. This method is sensitive to the formation and decomposition of a small amount of the $M\text{HgO}_2$ phase on the surface of alkaline-earth-oxide grains.

EXPERIMENTAL

The device for thermogravimetry under controlled oxygen and mercury partial pressures (Fig. 2) consists of a differential electronic balance, a temperature gradient tube furnace, and a recorder. A silica tube with a length 380–400 mm and an inner diameter 10 mm with substances under investigation was placed inside the furnace on the electronic balance shoulders. The temperature was measured with an accuracy of ±1 K. The accuracy of the mass measurement was ±0.001 g.

About 3 g HgO (99.9%) was placed in one part of a silica tube, while about 0.5 g CaCO_3 (99.9%), SrCO_3 (99.9%), or BaO_2 (99.9%) was placed into an alumina crucible in the other part of this tube. Then alkaline earth oxides were obtained by decomposition under heating in vacuum: CaCO_3 at 800°C, SrCO_3 at 1000°C, and BaO_2 at 900°C. After complete decomposition of starting carbonates or peroxide, the silica tube was evacuated, sealed, and placed on the balance shoulders. A mixture of $\text{Co}_3\text{O}_4/\text{CoO}$ was placed in the tube also for a three-temperature experiment. $M\text{HgO}_2$ has formed at $T^{(2)}$ during the experiments.

In order to determine the temperature $T_{\text{eq.}}^{(2)}$, at which $P(\text{Hg}) \cdot P(\text{O}_2)^{1/2} = K_{\text{p}(M\text{HgO}_2)}$, $T^{(2)}$ was increased at the rate of 0.5 K/min, while $T^{(1)}$ (as well as $T^{(3)}$ for the three-temperature variation) was kept constant, and the mass change as a function of $T^{(2)}$ was recorded. The typical patterns of cupola-shaped dependencies for two samples of CaHgO_2 are shown in Fig. 3. The mass of the sample $\text{CaO}/\text{CaHgO}_2$ increases first and then decreases due to formation of CaHgO_2 and its further decomposition. $T_{\text{eq.}}^{(2)}$ is defined as the temperature of the maximum mass of the $\text{CaO}/\text{CaHgO}_2$ sample where the mass transfer is absent. This technique was tested using HgO as a standard substance, replacing $M\text{O}/M\text{HgO}_2$ in the silica tube. The accuracy of the $T_{\text{eq.}}^{(2)}$ determination was estimated to be ±3 K.

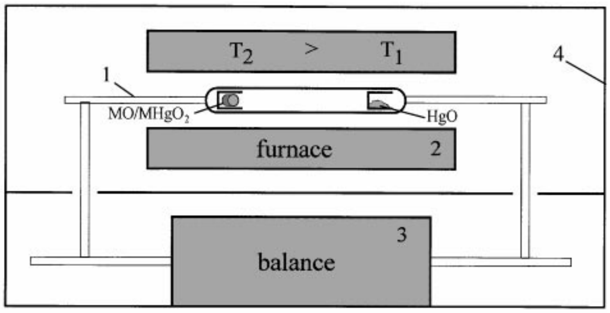

FIG. 2. Scheme of the thermogravimetric technique. 1, silica ampoule; 2, furnace with temperature gradient; 3, differential electronic balance; 4, cover.

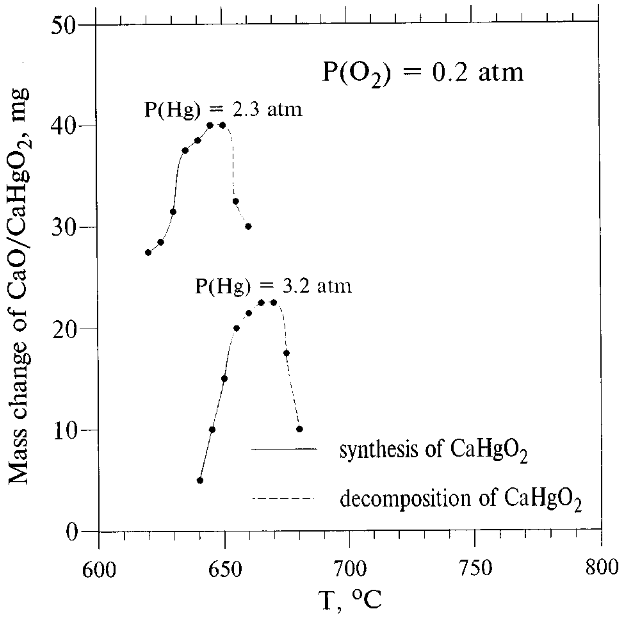

FIG. 3. The results of the thermogravimetric experiments for $CaHgO_2$.

RESULTS AND DISCUSSION

The thermodynamic equilibria of $CaHgO_2$, $SrHgO_2$, and $BaHgO_2$ with gas atmosphere were investigated at different mercury and oxygen partial pressures. Both techniques were used for $CaHgO_2$, whereas $SrHgO_2$ and $BaHgO_2$ were investigated by the two-temperature technique only.

$T^{(2)}_{eq.}$ was measured in wide ranges of mercury an oxygen partial pressures. The upper total pressure boundary was 10 atm, while the lower pressure boundary (1 atm) was limited by low rates of the $MHgO_2$ synthesis at low temperatures and pressures. The values of $P(Hg)$ and $P(O_2)$ and corresponding equilibrium constant $K_{p(MHgO_2)}$ were calculated for each $T^{(2)}_{eq.}$ as described above.

The total vapor pressures over $CaHgO_2$, $SrHgO_2$, $BaHgO_2$ versus temperature for the equilibrium Eq. [1] (three phase equilibrium $S(MHgO_2)S(MO)V$) together with reference data for HgO (10) are plotted in Fig. 4. The total vapor pressure for the reactions (Eq. [1]) at fixed temperature increases in order to $BaHgO_2$–$SrHgO_2$–$CaHgO_2$–HgO. Consequently, $BaHgO_2$ is the most stable substance upon heating in this row. This depedence is typical for thermal stability of inorganic salts containing alkaline earth metals, such as carbonates and nitrates.

The obtained $P_{total}(T)$ dependence for the $S(CaHgO_2)$ $S(CaO)V$ equilibrium for the pressure range 1–9 atm is in a good agreement with the same dependence from Ref. (7), determined for the range 9–27 atm.

In the case of $BaHgO_2$, it is necessary to take into consideration the possibility of BaO_2 formation at elevated oxygen pressures. According to Ref. (12), oxygen vapor pressure in the equilibrium $BaO_2 \Leftrightarrow BaO + 1/2O_2$ is described by the equation: $\log P[\text{MPa}] = -7406/T + 5.803$.

The determined $P(O_2)$ over $BaHgO_2$ is slightly smaller than over BaO_2 in the Ba–O system, and, moreover, the latter compound was not detected by X-ray analysis. Therefore, we can conclude that our data were not affected by a possible appearance of BaO_2. However, at higher $P(O_2)$ and lower T this problem should be taken into account.

The plots of $\log K_{p(MHgO_2)}$ vs $1/T$ for $CaHgO_2$, $SrHgO_2$, and $BaHgO_2$ are shown in Fig. 5, and the corresponding dependencies are described by a linear equation,

$$\log K_{p(MHgO_2)} = -\Delta_r H^\circ_T/2.303RT + \Delta_r S^\circ_T/2.303R,$$

where $\Delta_r H^\circ_T$ and $\Delta_r S^\circ_T$ are the average values of standard enthalpy and entropy of the reaction (Eq. [1]) for the experimental temperature intervals given in Table 1, $R = 8.314$ J/K · mole-gaseous constant.

The determined temperature dependencies of $K_{p(MHgO_2)}$ for $CaHgO_2$, $SrHgO_2$, and $BaHgO_2$ are described by the following equations:

$$\log K_p(CaHgO_2) = -(9424 \pm 540)/T + (10.28 \pm 0.57)$$
$$(888 \le T \le 1013\ \text{K}) \quad (\text{SD} = 0.07988,\ N = 9)$$

$$\log K_p(SrHgO_2) = -(10197 \pm 890)/T + (10.10 \pm 0.83)$$
$$(1043 \le T \le 1118\ \text{K}) \quad (\text{SD} = 0.06767,\ N = 12)$$

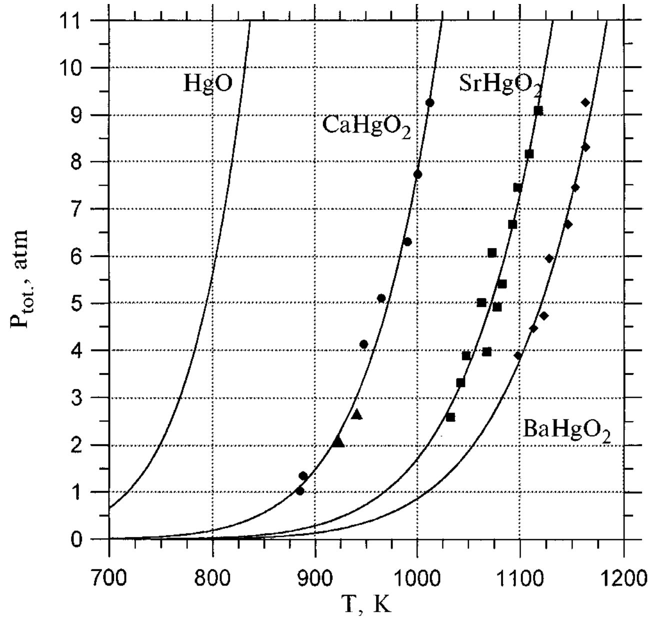

FIG. 4. The total vapor pressure (P_{total}) dependence vs temperature for the $S(MHgO_2)$ $S(MO)V$ equilibrium at $P(Hg) = 2P(O_2)$ for: $CaHgO_2$ (▲, three- and ●, two-temperature variations), $SrHgO_2$, $BaHgO_2$. HgO, references data (10).

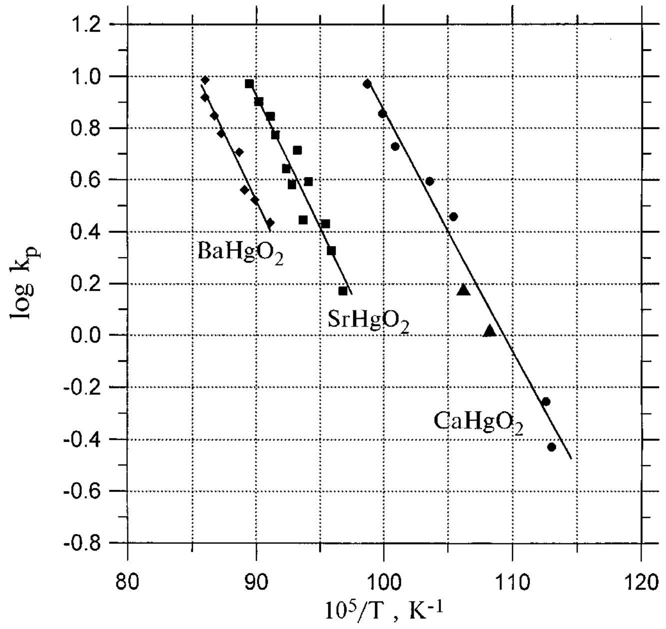

FIG. 5. The dependencies of $\log K_p(M\text{HgO}_2)$ vs $1/T$ for the equilibrium $M\text{HgO}_2\text{(s)} \Leftrightarrow M\text{O(s)} + \text{Hg(v)} + 1/2\text{O}_2$ for CaHgO_2 (▲, three- and ●, two-temperature variations), SrHgO_2, and BaHgO_2.

$$\log K_p(\text{BaHgO}_2) = -(10474 \pm 730)/T + (9.94 \pm 0.64)$$

$$(1098 \leq T \leq 1163\ \text{K}) \quad (\text{SD} = 0.03772,\ N = 9),$$

where SD is the standard deviation of $\log K_p$ and N is the number of experimental points.

The calculated average values of $\Delta_r H^\circ_T$ and $\Delta_r S^\circ_T$ for the reaction (Eq. [1]) are given in Table 1. The standard enthalpy $\Delta_r H^\circ_{298}$ and entropy $\Delta_r S^\circ_{298}$ of the reactions were estimated using the assumption that the heat capacity of $M\text{HgO}_2$ is equal to the sum of heat capacities of oxides MO(s) and HgO(s). The experimental data of heat capacities measurements for CaHgO_2 and BaHgO_2 in the range of 193–600 K (6) confirm this assumption. The values of heat capacities of monoxides were taken from Ref. (10).

The obtained enthalpy of the reaction Eq. [1] for BaHgO_2 (200 ± 14 kJ/mole) is in good agreement with the value obtained by the TG-DSC technique (200 ± 8 kJ/mole), while there is some deviation of our value for CaHgO_2 (180 ± 10 kJ/mole) from the literature data (160 ± 9 kJ/mole) (6) and 138 kJ/mole (7). These differences can be caused by the limitations of the TG-DSC and TBA techniques, which are discussed above, and different temperature intervals in our and TBA measurements.

The calculated values of standard enthalpies $\Delta_{ox}H^\circ_{298}$ and entropies $\Delta_{ox}S^\circ_{298}$ of the $M\text{HgO}_2$ formation from oxides MO(s) and HgO(s) are presented in Table 2. These data were obtained using the reference data (10) for the reaction: $\text{Hg(v)} + 1/2\text{O}_2 = \text{HgO(s)}(\Delta_r H^\circ_{298} = -152.09 \pm 0.12$ kJ/mole, $\Delta_r S^\circ_{298} = -207.11 \pm 0.13$ J/K · mole). The obtained values of $\Delta_{ox}S^\circ_{298}$ are close to zero. This fact is an indirect confirmation of the reliability of the obtained values, as the entropy change in solid state reactions without vapor phase should be a small value.

The standard enthalpies of formation of mercurates from the elements $\Delta_f H^\circ_{298}$ and the absolute entropies S°_{298} of $M\text{HgO}_2$ presented in Table 2 were calculated using the references data from (10): CaO–$\Delta_f H^\circ_{298} = -635.09 \pm 0.88$ kJ/mole, $S^\circ_{298} = 38.21 \pm 0.13$ J/K · mole; SrO–$\Delta_f H^\circ_{298} = -592.04 \pm 3.35$ kJ/mole, $S^\circ_{298} = 55.52 \pm 0.42$ J/K · mole; BaO–$\Delta_f H^\circ_{298} = -548.10 \pm 2.09$ kJ/mole, $S^\circ_{298} = 72.17 \pm 0.38$ J/K · mole, and HgO–$\Delta_f H^\circ_{298} = -90.79 \pm 0.10$ kJ/mole, $S^\circ_{298} = 70.27 \pm 0.13$ J/K · mole).

The obtained data of vapor pressure over CaHgO_2 and BaHgO_2 can be used for the optimization of the synthesis of Hg-based superconductors. The dependence of mercury partial vapor pressure over $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201 phase) vs temperature and $P(\text{O}_2)$ is expressed by

$$\log P(\text{Hg, atm}) = -6040/T(\text{K}) - 0.266 \log P(\text{O}_2, \text{atm}) + 5.959 \text{ (Ref. (8))}$$

for the $S(\text{HgBa}_2\text{CuO}_{4+\delta})\ S(\text{Ba}_2\text{CuO}_{3+x})\text{V}$ equilibrium.

The dependence of P(Hg) over BaHgO_2 in equilibrium (Eq. [1]) vs temperature and $P(\text{O}_2)$ is described by the following equation:

$$\log P(\text{Hg, atm}) = -10474/T(\text{K}) - 0.5 \log P(\text{O}_2, \text{atm}) + 9.94.$$

TABLE 1
The Values of Enthalpy and Entropy for the Reaction $M\text{HgO}_2\text{(s)} \Leftrightarrow M\text{O(s)} + \text{Hg(v)} + 1/2\text{O}_2$

Alkaline-earth metal	Temperature range, K	$\Delta_r H^\circ_T$ kJ/mole	$\Delta_r S^\circ_T$ J/K · mole	$\Delta_r H^\circ_{298}$ kJ/mole	$\Delta_r S^\circ_{298}$ J/K · mole
Ca	888–1013	180 ± 10	197 ± 11	191 ± 10	215 ± 11
Sr	1043–1118	195 ± 17	193 ± 16	209 ± 17	214 ± 16
Ba	1098–1163	200 ± 14	190 ± 12	215 ± 14	212 ± 13

TABLE 2
The Values of Enthalpy and Entropy of the $M\text{HgO}_2$ Formation from Oxides and from Elements

No.	Compound	$\Delta_{ox}H^\circ_{298}$ kJ/mole	$\Delta_{ox}S^\circ_{298}$ J/K · mole	$\Delta_f H^\circ_{298}$ kJ/mole	S°_{298} J/K · mole
1	CaHgO_2	− 39 ± 10	− 8 ± 11	− 765 ± 10	101 ± 11
2	SrHgO_2	− 57 ± 17	− 7 ± 16	− 740 ± 17	119 ± 16
3	BaHgO_2	− 63 ± 14	− 5 ± 13	− 701 ± 14	138 ± 13

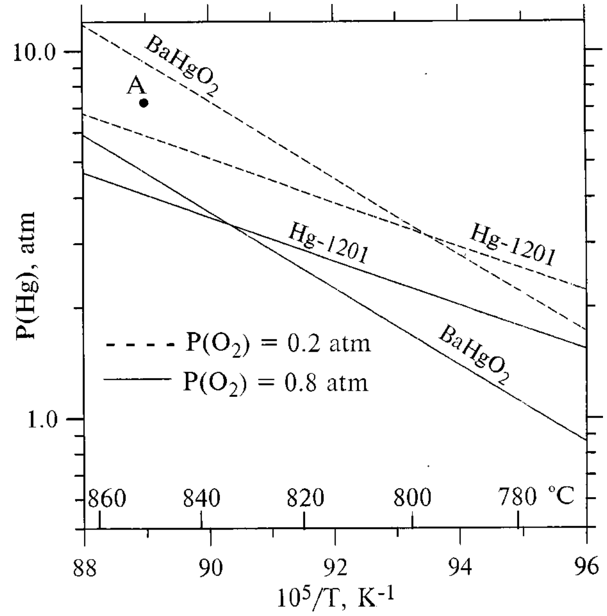

FIG. 6. The dependencies of $P(Hg)$ vs T at $P(O_2) = 0.2$ and 0.8 atm for the equilibria $S(BaHgO_2)S(BaO)V$ and $S(HgBa_2CuO_{4+\delta})S(Ba_2CuO_{3+x})V$ (Ref. (8)).

These dependencies $(P(Hg)) = f(T)$ for $HgBa_2CuO_{4+\delta}$ and $BaHgO_2$ are plotted in Fig. 6 for $P(O_2) = 0.2$ and 0.8 atm. By analyzing such type of diagrams one can choose the optimal synthesis conditions for $HgBa_2CuO_{4+\delta}$.

As seen from Fig. 6, the stability fields of these two phases ($BaHgO_2$ and $HgBa_2CuO_{4+\delta}$) depend strongly on the partial oxygen pressure. Let us consider the equilibrium corresponding to the point **A** ($P(Hg) = 7$ atm, $T = 850°C$), for instance. At $P(O_2) = 0.8$ atm both phases are thermodynamically stable and coexist in equilibrium with gaseous phase. However, at lower oxygen pressure (0.2 atm) only $HgBa_2CuO_{4+\delta}$ is stable, while $BaHgO_2$ does not form. Therefore, synthesis of $HgBa_2CuO_{4+\delta}$ at $P(O_2) = 0.2$ atm is more favorable, since it allows to avoid the formation of $BaHgO_2$ as a possible impurity phase. At lower oxygen pressure inside the reaction vessel a larger temperature range can be chosen for the synthesis of Hg-1201. Earlier (13) we have shown that synthesis of monophase Hg-1201 samples is indeed much more successful if it is performed at $P(O_2) \leq 0.2$ atm.

Similar conclusions can be made for the synthesis of $HgBa_2CaCu_2O_{6+\delta}$ and $HgBa_2Ca_2Cu_3O_{8+\delta}$ when thermodynamic data are available and compared with the data for $CaHgO_2$ obtained in the present work.

CONCLUSION

The novel technique of thermogravimetry under controlled mercury and oxygen partial pressures was developed to investigate the phase equilibria $MHgO_2(s) \Leftrightarrow MO(s) + Hg(v) + 1/2O_2$ (M = Ca, Sr, and Ba). Two modifications of this method allowed us to determine the total vapor pressures for these equilibria and to calculate the enthalpy and entropy values of the reactions, as well as the standard values of enthalpy and entropy of $CaHgO_2$, $SrHgO_2$, and $BaHgO_2$ formation from oxides and from elements. It was found that the thermal stability increases in the order $CaHgO_2$, $SrHgO_2$, $BaHgO_2$.

ACKNOWLEDGMENT

This work was partially supported by the Swiss National Science Foundation (7SUPJ 048713), Russian State Program on Superconductivity (POISK-4), and Russian Foundation for Basic Research (98-03-32700a). D.A.M. acknowledges the ISSEP (a98-1842).

REFERENCES

1. S. N. Putilin, E. V. Antipov, O. Chmaissem, and M. Marezio, *Nature* **362,** 226 (1993).
2. A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, *Nature* **363,** 56 (1993).
3. O. Chmaissem, Q. Huang, S. N. Putilin, M. Marezio, and A. Santoro, *Physica C* **212,** 259 (1993).
4. M. Soll and H. Müller-Buschbaum, *J. Less-Common Metal.* **162,** 169 (1990).
5. S. N. Putilin, S. M. Kazakov, and M. Marezio, *J. Solid State Chem.* **109,** 406 (1994).
6. M. V. Gorbacheva, A. F. Mayorova, S. N. Mudretsova, and M. L. Kovba, *in* "Proceedings of Russian conference on thermal analysis and calorimetry, Kazan, Russia," p. 138, 1996.
7. A. Sin, A. G. Cunha, A. Calleja, M. T. D. Orlando, F. G. Emmerich, E. Baggio-Saitovich, S. Pinol, J. M. Chimenous, and X. Obradors, *Physica C* **306,** 34 (1998).
8. V. A. Alyoshin, D. A. Mikhailova, and E. V. Antipov, *Physica C* **271,** 197 (1996).
9. An. N. Nesmeyanov, Vapor pressure of chemical elements, Moscow, AN USSR Publ., p. 24, 1961. [in Russian]
10. JANAF Thermochemical Tables, NBS USA, Washington, 1971–1975.
11. M. V. Gorbacheva, A. F. Mayorova, S. N. Mudretsova, E. B. Rudnyi, and A. D. Rusin, *Zhurnal Fizicheskoi Khimii* **72,** 416 (1998). [In Russian]
12. I. L. Aptekar, A. V. Kosenko, A. A. Zhochov, V. M. Masalov, and G. A. Emel'yanchenko, *Sverchprovodimost* **4,** 801 (1991). [In Russian]
13. V. A. Alyoshin, D. A. Mikhailova, and E.V. Antipov, *Physica C* **255,** 173 (1995).