Gibbs Free Energy of Formation of $Eu_{1+y}Ba_{2-y}Cu_3O_{7-x}$ and Related Phases in the Eu_2O_3–CuO–BaO System

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The Gibbs energies of formation of the ternary phases in the Eu–Ba–Cu–O system have been obtained from solid state electrochemical measurements in the temperature range 973 to 1173 K. Cells employing single-crystal calcium fluoride as an electrolyte were used in studies of $CuBaO_2$, Eu_2CuBaO_5, and $Eu_{1+y}Ba_{2-y}Cu_3O_{7-x}$ ($y = 0, 0.5$). Based on the results of emf measurements the standard Gibbs free energy of formation of respective phases from the constituent oxides was derived. © 1996 Academic Press, Inc.

1. INTRODUCTION

The atomic size of the lanthanide, Ln, has profound effect on the trend of phase and solid solution formation as well as phase relations in the CuO-rich part of the Ln_2O_3–CuO–BaO systems. For $Ln = La \ldots Gd$, $CuLa_2O_4$ is present in the CuO–Ln_2O_3 system and it is replaced by $Cu_2Ln_2O_5$ for $Ln = Dy \ldots Lu$. This change is accompanied with the relocation of tie-lines in the ternary field. It was shown by Wong-Ng *et al.* (1) that for the smaller lanthanide atoms (Gd to Yb, and Y) the $LnBa_2Cu_3O_{7-x}$ phase (denoted further as $\langle 123 \rangle$) is in equilibrium with CuO and Ln_2BaCuO_5 ("green phase," denoted further as $\langle 211 \rangle$) in the CuO-rich portion of the Ln_2O_3–CuO–BaO phase diagram. However, for the larger lanthanide atoms (La to Eu) the $\langle 123 \rangle$ solid solution is in equilibrium with CuO and $CuLn_2O_4$ phases in this region of the phase diagram. The solid solution of $Ln_{1+y}Ba_{2-y}Cu_3O_{7-x}$ may extend from the composition of the superconducting phase $\langle 123 \rangle$ with $y = 0$ to the composition as high as $Ln_{1.7}Ba_{1.3}Cu_3O_{7-x}$ in the case of $Ln = La$ ($y = 0.7$). These changes in phase relations reflect a change in thermodynamic properties of the respective phases with changes in the atomic size of the lanthanide. Unfortunately, except for a relatively large amount of information about the thermodynamic stability of respective phases existing in the Y-Ba-Cu-O system (2, 3, 4) this kind of information is generally missing as far as other lanthanide systems are concerned.

Since it seems that either europium or gadolinium is the element for which the change in general trends of phase relationship is observed in the systems discussed above, it was decided to investigate the thermodynamic stability of phases based on europium oxide. Phase relations in the Eu_2O_3–CuO–BaO system are schematically shown in Fig. 1.

Instead of stoichiometric $\langle 123 \rangle$ phase, a solid solution $Eu_{1+y}Ba_{2-y}Cu_3O_{7-x}$ ranging from $y = 0$ to $y = 0.5$ exists. According to the phase diagram studies of Hodorowicz *et al.* (5) and Pieczulewski *et al.* (6) this phase appears to be in equilibrium with CuO and $\langle 211 \rangle$ phase. In the present work electrochemical cells with single-crystal CaF_2 solid electrolytes were used to measure emf's from which the respective Gibbs free energy changes of subsequent reactions of formation of those Eu-phases were calculated.

2. EXPERIMENTAL

a. Sample Preparation

Conventional ceramic methods were used to prepare $CuBaO_2$, Eu_2BaCuO_5 (designated as $\langle 211 \rangle$), $EuBa_2Cu_3O_{7-x}(\langle 123 \rangle)$, and $Eu_{1.5}Ba_{1.5}Cu_3O_{6+x}(\langle 336 \rangle)$. Weighed amounts of powders of $BaCO_3$ (reagent grade) obtained from POCh, Gliwice (Poland), Eu_2O_3 (99.9%) obtained from Aldrich Chemicals Co. (USA), and CuO (99.999%) obtained from Johnson Matthey (USA) were mixed, pelletized, and sintered under a stream of dry oxygen at about 1223 K. Before sample preparation europium oxide was annealed at 1273 K under a stream of pure oxygen, and $BaCO_3$ was dried in argon at 873 K. The procedure of intermediate grinding, mixing, and pelletizing was repeated three times. The compound $CuBaO_2$ was prepared from an equimolar mixture of CuO and $BaCO_3$ at 1113 K. The compound $CuEu_2O_4$ was prepared in a similar manner from an equimolar mixture of CuO and Eu_2O_3 at 1273 K. The electrode pellets were prepared by mixing these compounds with BaF_2 and then sintering at 1173 K under a stream of dry oxygen. $CaO + CaF_2$ reference electrodes were made from equimolar amounts of the components in two steps. First, the pellets were sintered at 1273 K under argon for 24 h, and then after intermediate
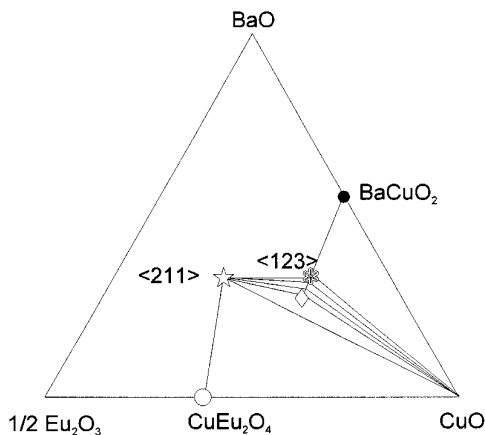
FIG. 1. Schematic diagram of phase equilibria in the CuO-rich corner of the Eu$_2$O$_3$–CuO–BaO system.

regrinding they were sintered again at 1173 K under dry oxygen for another 24 h.

b. Technique

The application of CaF$_2$-type electrolyte for thermodynamic study of oxide compounds has been discussed by Levitskii (7). The cell construction in this study followed that used by Alcock and Li (8) in the study of the thermodynamic properties of the Cu–Sr–O system. The electrochemical cell used in our work is schematically shown in Fig. 2.

The cell was placed in a horizontal resistance furnace. The temperature was controlled by an Omega CR9700 temperature controller. The temperature was measured with a Pt-PtRh10 thermocouple. Dry, synthetic air (Linde, Germany), which was virtually water-free, was flowed con-

tinuously through the cell vessel. The emf was measured with a Keithley 197A microvolt DMM. The equilibrium emf values were attained in 3 to 10 h, depending on temperature. The cell resistance was of order 10 kΩ in the temperature range from 973 to about 1100 K. The platinum lead wires did not show signs of reaction with the electrode pellets after the experiments. The emf measurements were carried out in several cycles of increasing and decreasing temperature. The whole experimental cycle of the cell operation usually took about one week.
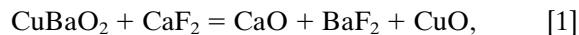
3. RESULTS

a. Gibbs Free Energy of Formation of CuBaO$_2$

The cell

$$\text{air, CaO + CaF}_2\|\text{CaF}_2\|\text{CuO + CuBaO}_2\text{ + BaF}_2\text{, air} \quad \text{[I]}$$
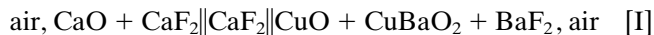
was used to determine the change in Gibbs free energy of the net cell reaction

$$\text{CuBaO}_2\text{ + CaF}_2 = \text{CaO + BaF}_2\text{ + CuO,} \quad \text{[1]}$$

which is calculated directly from the cell emf using the relationship

$$\Delta G^0_{(1)} = -2FE_\text{I}. \quad \text{[2]}$$

The emf results, shown in Fig. 3, can be expressed as

$$E_\text{I}(\text{mV}) = 146.0 - 0.0376 \cdot T(\pm 1.5) \quad \text{[3]}$$

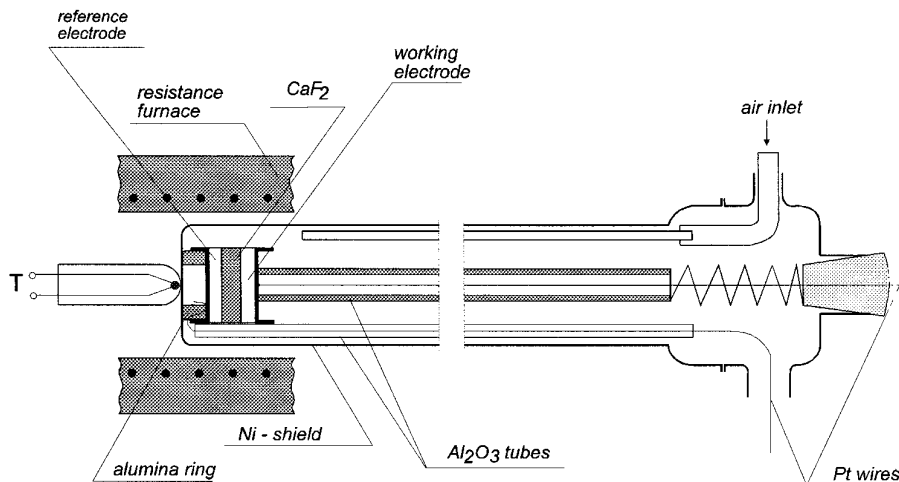and the corresponding change in Gibbs free energy of reaction [1] is given by

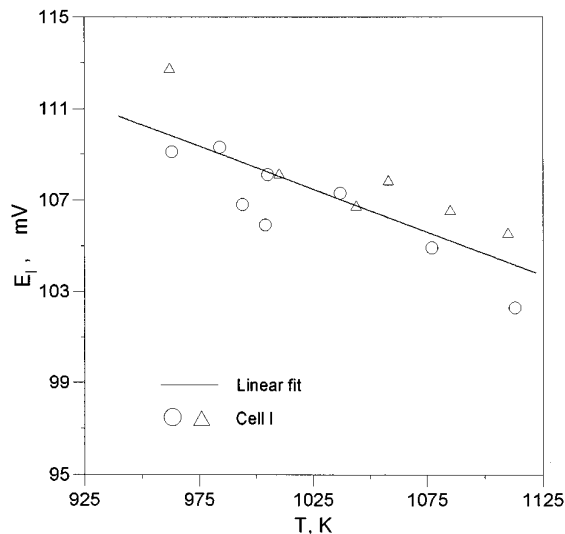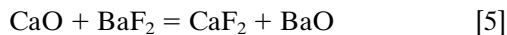
FIG. 2. Schematic diagram of the electrochemical cell.

FIG. 3. Variation of emf with temperature for cell I. (○) first run, (△) second run.

$$\Delta G^0_{(1)}(J) = -28200 + 7.26 \cdot T(\pm 870). \qquad [4]$$

We have analyzed the literature data for the exchange reaction

$$CaO + BaF_2 = CaF_2 + BaO \qquad [5]$$

and have accepted the change in Gibbs free energy as given by Kaye and Laby (9), which is

$$\Delta G^0_{(5)}(J) = 63785 - 3.77 \cdot T(\pm 1000). \qquad [6]$$

Combining reactions [1] and [5] gives the formation reaction

$$BaO + CuO = CuBaO_2 \qquad [7]$$

and combining the thermodynamic data in [4] and [6] gives the change in Gibbs free energy for reaction [7] as

$$\Delta G^0_{(7)}(J) = -35600 - 3.5 \cdot T(\pm 1300). \qquad [8]$$

The change in Gibbs free energy of reaction [7] is found to be in very good agreement with other experimental data (10–13).

b. Gibbs Free Energy of Formation of Eu_2BaCuO_5 ($\langle 211 \rangle$)

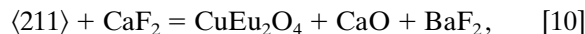The following electrochemical cell was assembled:

air, $CaO + CaF_2 \| CaF_2 \| CuEu_2O_4 + \langle 211 \rangle + BaF_2$, air. [II]
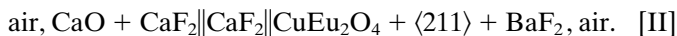
The variation of the emf with temperature of cell II is shown in Fig. 4. The linear relation between emf and temperature is

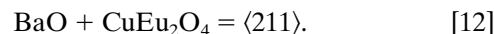$$E_{II}(mV) = -101.7 + 0.1109 \cdot T(\pm 2.0). \qquad [9]$$

For cell II, the net reaction can be written as

$$\langle 211 \rangle + CaF_2 = CuEu_2O_4 + CaO + BaF_2, \qquad [10]$$

which yields the change in Gibbs free energy for reaction [10] in the form

$$\Delta G^0_{(10)}(J) = -2FE_{II} = 19630 - 21.4 \cdot T(\pm 1100). \qquad [11]$$

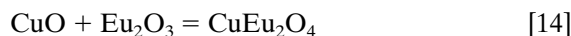Combining reactions [10] and [5] the following reaction of formation of $\langle 211 \rangle$ is obtained:

$$BaO + CuEu_2O_4 = \langle 211 \rangle. \qquad [12]$$

The corresponding expression for the change in Gibbs free energy of reaction [12] is

$$\Delta G^0_{(12)}(J) = -83420 + 25.2 \cdot T(\pm 1500). \qquad [13]$$

Next, using the change in Gibbs free energy determined previously (14) for the reaction,

$$CuO + Eu_2O_3 = CuEu_2O_4 \qquad [14]$$

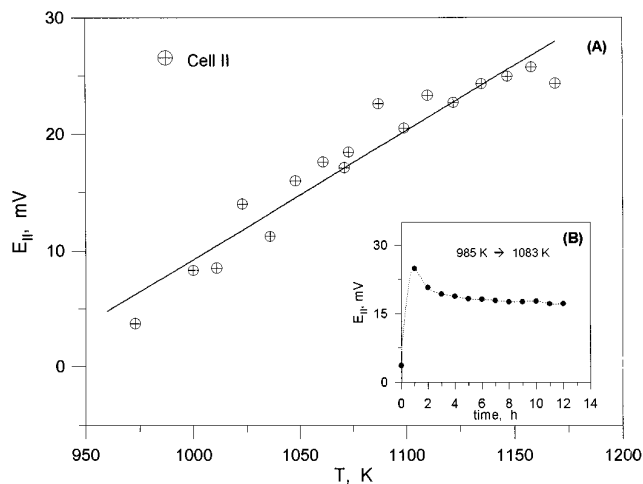$$\Delta G^0_{(14)}(J) = 885 - 8.67 \cdot T(\pm 1000), \qquad [15]$$

FIG. 4. Variation of emf with temperature of cell II (A), and an example of the variation of emf with time after the temperature change (B).
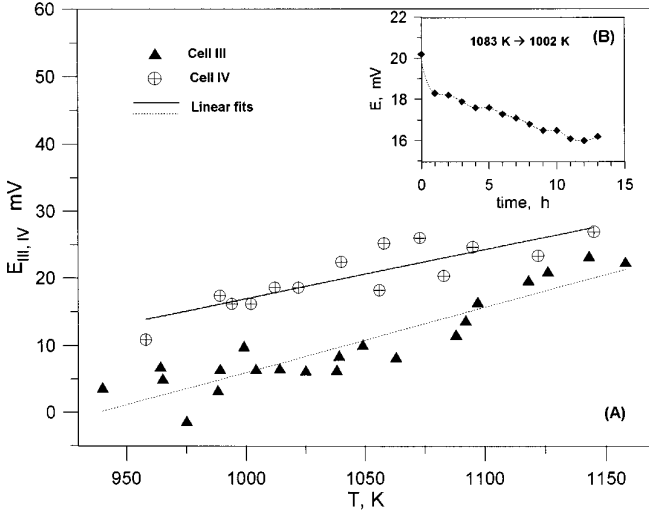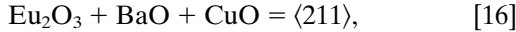
FIG. 5. Variation of emf with temperature of cells III and IV (A), and an example of the emf variation with time after the temperature change in cell IV (B).

one can derive the Gibbs free energy change of the reaction of formation of the $\langle 211 \rangle$ phase from the oxides,
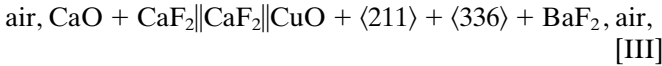
$$Eu_2O_3 + BaO + CuO = \langle 211 \rangle, \qquad [16]$$

in the following form:

$$\Delta G^0_{(16)}(J) = -82530 + 16.5 \cdot T(\pm 1800). \qquad [17]$$

c. Gibbs Free Energy of Formation of
   $Eu_{1+y}Ba_{2-y}Cu_3O_{7-x}$ for $y = 0.5$

Since the composition of the $Eu_{1+y}Ba_{2-y}Cu_3O_{7-x}$ phase ranges from $y = 0$ ($\langle 123 \rangle$) to $y = 0.5$ ($\langle 336 \rangle$), a cell was assembled to measure the change in Gibbs free energy of formation of $\langle 336 \rangle$,

$$\text{air, } CaO + CaF_2 \| CaF_2 \| CuO + \langle 211 \rangle + \langle 336 \rangle + BaF_2, \text{ air,} \qquad [III]$$

for $y = 0.5$. The variation of emf with temperature for cell III is shown in Fig. 5.

The linear relation between emf and temperature for cell III is

$$E_{III}(mV) = -90.8 + 0.0968 \cdot T(\pm 2.8). \qquad [18]$$

Since nothing is known about the oxygen stoichiometry of $\langle 336 \rangle$ we assumed that this phase is stoichiometric with respect to oxygen. The net reaction of cell III is written as

$$4\langle 336 \rangle + 3\, CaF_2 = 3\langle 211 \rangle + 9\, CuO + 3\, CaO + 3\, BaF_2 \quad [19]$$
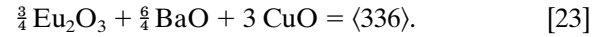
with the corresponding change in Gibbs free energy

$$\Delta G^0_{(19)} = -6\, FE_{III}. \qquad [20]$$

Taking into account the exchange reaction [5] one obtains for the formation reaction

$$\tfrac{3}{4}\langle 211 \rangle + \tfrac{3}{4} BaO + \tfrac{9}{4} CuO = \langle 336 \rangle \qquad [21]$$
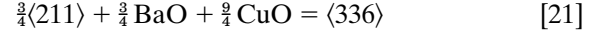
$$\Delta G^0_{(21)}(J) = -60\,980 + 16.84 \cdot T(\pm 5000). \qquad [22]$$

Combining reaction [21] with reaction [16] yields the formation of $\langle 336 \rangle$ from the oxides:

$$\tfrac{3}{4} Eu_2O_3 + \tfrac{6}{4} BaO + 3\, CuO = \langle 336 \rangle. \qquad [23]$$

$$\Delta G^0_{(23)}(J) = -122\,880 + 29.22 \cdot T(\pm 5500). \qquad [24]$$

4. DISCUSSION

The performance of our emf cell with CaF_2 electrolyte was checked by comparing the measured change in Gibbs free energy of reaction, $BaO + CuO = CuBaO_2$ (reaction [7]), with available literature data. The change in Gibbs free energy of reaction [7] was determined by Borowiec and Kolbrecka (10), Pashin and Tretyakov (11), Fan *et al.* (12), and Shimpo and Nakamura (13). Results produced by emf cells with zirconia (10), CaF_2 (12), and BaF_2 (11) solid electrolytes are very close to one another as well as to those of our study, though they all differ slightly in temperature dependence. The thermogravimetric study of Shimpo and Nakamura (13) yielded the ΔG^0 values higher of about 10 kJ. The close agreement of our data for reaction [7] (which requires thermodynamic data for reaction [5]) with the direct measurements of the change in Gibbs free energy in (10, 11, 12) show that the thermodynamic data we selected for reaction [5] are correct. The results of Azad *et al.* (15) are found to be much lower (Fig. 6). We speculate that the reason for so large a discrepancy is the performance of the $BaZrO_3 + ZrO_2 + BaF_2$ reference electrode used in study (15).

It is worth mentioning that we also employed the cell

$$\text{air, } CaO + CaF_2 \| CaF_2 \| CuO + \langle 211 \rangle + \langle 123 \rangle + BaF_2, \text{ air} \qquad [IV]$$
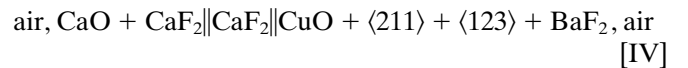
for $y = 0$.

The variation of emf with temperature for cell IV is shown in Fig. 5. It can be represented by the linear relation

$$E_{IV}(mV) = -56.1 + 0.0731 \cdot T(\pm 2.4). \qquad [25]$$
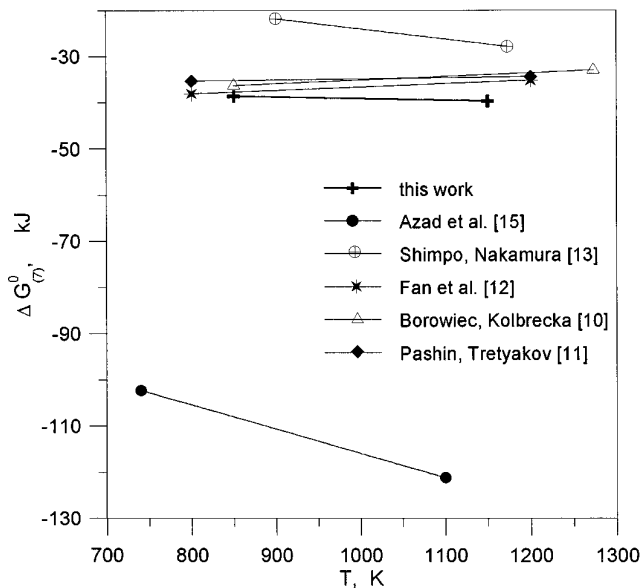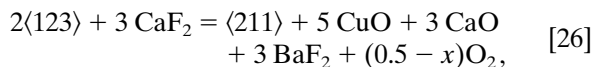
Assuming the net cell reaction

FIG. 6. Temperature dependence of ΔG_T^0 for the reaction [7].

$$2\langle 123\rangle + 3\,CaF_2 = \langle 211\rangle + 5\,CuO + 3\,CaO$$
$$+\ 3\,BaF_2 + (0.5 - x)O_2, \qquad [26]$$

the change in Gibbs free energy for this reaction can be calculated as

$$\Delta G_{(26)}^0 = -6\,FE_{IV} - (0.5 - x)\cdot RT\ln p_{O_2}. \qquad [27]$$

The $p_{O_2} - T - x$ dependence determined for $\langle 123\rangle$ in our previous work (16) allowed the term $(0.5 - x)\cdot R\cdot\ln p_{O_2}$ to be evaluated as a function of temperature for the partial pressure of oxygen in air. Consequently, the change in Gibbs free energy for the formation of one mole of $\langle 123\rangle$ from the oxides and oxygen,

$$\tfrac{1}{2}Eu_2O_3 + 3\,CuO + 2\,BaO + (0.5 - x)\tfrac{1}{2}O_2 = \langle 123\rangle, \qquad [28]$$
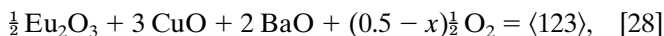
can be calculated as

$$\Delta G_{(28)}^0(J) = -163\,250 + 44.7\cdot T(\pm 3500). \qquad [29]$$

However this result should be taken with caution. On one hand, the cell IV operated reversibly for five days showing no sign of the side reaction. On the other, it seems that according to known phase diagrams (5, 6) three phases, CuO, $\langle 211\rangle$, and $\langle 123\rangle$, should not coexist simultaneously. Since the investigated electrode consists of a mixture of four phases it is possible that the kinetics of processes in the solid state is responsible for observed cell behavior. Better assessment of the reliability of the data derived

from the results of cell IV will be possible when more data on the stability of $Ln\langle 123\rangle$ compounds become available.

Our results obtained for $\langle 211\rangle$, $\langle 123\rangle$, and $\langle 336\rangle$ can be compared with similar values determined for the respective yttrium compounds. As far as Y_2BaCuO_5 is concerned, the calorimetric studies of Zhou and Navrotsky (17), Morss *et al.* (18), and Garzon *et al.* (19) gave values of the enthalpy of formation from oxides, -59.2 at 977 K, and -92.0 and -76.2 kJ/mol at room temperature, respectively. Corresponding enthalpies derived from emf studies are more diverse. These values vary from -24.4 (12) to -152.5 kJ/mol (20), while other results lie just between -72.5 (21) and -61.7 kJ/mol (11). In the case of $YBa_2Cu_3O_{7-x}$, Zhou and Navrotsky (17) found that the enthalpy of formation from oxides depends on oxygen content, $(7 - x)$. According to their study it varies from -74.2 for the oxygen deficient compound to -106.2 kJ/mol for the oxygen saturated compound. Morss *et al.* (22) reported the value -126.0 kJ/mol for the oxygen saturated sample at room temperature. Corresponding enthalpy values derived from emf's vary from -53.0 (11) through -109.0 (12) to -210.6 kJ/mol (15).

Comparing our new enthalpy of formation values derived for respective europium compounds from emf measurements ($\langle 211\rangle$, -82.5 kJ/mol; $\langle 123\rangle$, -163.3 kJ/mol; $\langle 336\rangle$, -122.9 kJ/mol) with those listed above for yttrium compounds, one can conclude they are all in the similar range. Better agreement can not be expected because of still significant discrepancies observed for yttrium compounds and the fact that europium compounds may exhibit different thermodynamic properties than those of yttrium.

The change in the Gibbs free energy of formation of the various phases from the oxides is shown in Fig. 7. The
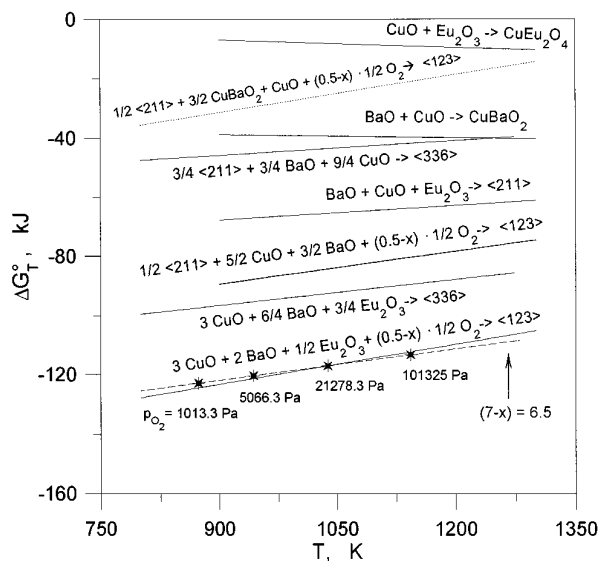

FIG. 7. Gibbs free energy change of formation of binary and ternary oxide phases from simple oxides.

dashed line corresponds to the calculated free energy of formation of ⟨123⟩ with $(7 - x) = 6.5$ stoichiometry. This process can be accomplished only by simultaneous setting temperature and p_{O_2}. On one hand, it is seen that at high temperature pressures above 101325 Pa O$_2$ are needed to keep the 6.5 value, since the natural tendency drives oxygen out, producing the stoichiometry $(7 - x) < 6.5$. On the other hand, decreasing temperature requires a simultaneous decrease of p_{O_2} to keep the 6.5 value constant, while the natural tendency is to produce the ⟨123⟩ phase with $(7 - x) > 6.5$. These findings are compatible with the process observed in practice.

According to the study of Wong-Ng *et al.* (1) phase diagrams with lanthanide oxides can be classified into two groups, one where ⟨123⟩ coexists with CuO and ⟨211⟩, and another where ⟨123⟩-based solid solution coexists with CuO and CuLn_2O$_4$. The element with which this change of trend occurs is either Gd or Eu. In order to explain the observed changes in phase relations the systematic study of thermodynamic properties of subsequent lanthanide compounds is needed. Results of such a study may help to predict temperature evolution of phase equilibria in any of those systems.

ACKNOWLEDGMENTS

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