

Gibbs Free Energy of Formation of Ln_2CuBaO_5 Compounds Determined by the EMF Method ($Ln = Yb, Tm, Er, Ho, Dy, \text{ and } Gd$)

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Employing electrochemical cells with calcium fluoride solid electrolyte

air,

$CuO + Ln_2Cu_2O_5 + Ln_2CuBaO_5 + BaF_2 // CaF_2 // CaO + CaF_2,$
air

for $Ln = Yb, Er, Tm, Ho, Dy, \text{ and}$

air,

$CuGd_2O_4 + Gd_2CuBaO_5 + Gd_2O_3 + BaF_2 // CaF_2 // CaO + CaF_2,$
air,

the Gibbs free energy change of the reaction of formation of the solid Ln_2CuBaO_5 “green” phase for subsequent lanthanide elements was determined. Obtained results were used to derive Gibbs free energy change of reactions of formation of respective Ln_2CuBaO_5 phases from constituent oxides. © 1997 Academic Press

1. INTRODUCTION

The discovery of a 30-K La–Ba–Cu oxide superconductor by Bednorz and Muller (1) stimulated an intense search for higher T_c materials of that kind. It was soon discovered (2) that new oxide superconductor with T_c above 90 K exists in the quaternary Y–Ba–Cu–O system, and the substitution of yttrium by lanthanide elements creates a whole family of similar compounds. The precise knowledge of phase equilibria and thermodynamic stability of respective phases in terms of temperature and oxygen potential is required to define processing conditions of these materials. Unfortunately, except for relatively large amount of information about thermodynamic stability of phases existing in the Y–Ba–Cu–O system (3–5), there is virtually no data for similar compounds with lanthanide elements in respective quaternary systems. This loss of interest can be explained to certain extent by the shift of research efforts due to the discovery of the high T_c oxide superconductor in the Bi–Sr–Ca–Cu–O ($\langle 2212 \rangle$ phase) system. Consequently, this system has received more attention recently, leaving the

chemistry of Ln –Ba–Cu–O systems open for further exploration. The systems of Ln –Cu–Ba–O type, however, are easier to investigate as far as thermodynamic stability of respective phases existing in these systems is concerned since their phase relations are better known.

Because the understanding of correlations between dimensions of the lanthanide ions, phase equilibria, and thermodynamic properties of respective phases still requires new data, attempts have been made to enlarge this kind of information. In the previous paper (6) we have studied stability of phases existing in the Eu–Ba–Cu–O system. The system with europium is interesting since Eu is the element which apparently divides Ln –Ba–Cu–O systems into two groups: with and without solid solution based on superconducting $\langle 123 \rangle$ phase (7). We have also recently reinvestigated Gibbs free energy of formation of double oxides in CuO – Ln_2O_3 systems for elements $Ln = Yb, Tm, Er, Ho, Dy, \text{ and } Gd$ (8). In this work we have determined the Gibbs free energy of formation of Ln_2BaCuO_5 compounds (“green phase”) for the same elements using an EMF cell with calcium fluoride solid electrolyte.

2. EXPERIMENTAL

a. Sample Preparation

Conventional ceramic methods were used to prepare Ln_2CuBaO_5 (designated as $Ln\langle 211 \rangle$) phase for $Ln = Yb, Tm, Er, Ho, Dy \text{ and } Gd$. Weighed amounts of powders of $BaCO_3$ (reagent grade) obtained from POCh, Gliwice (Poland) and CuO (99.999%) obtained from Johnson and Matthey (U.S.A.) were mixed with respective lanthanide oxides, pelletized, and sintered in a stream of dry oxygen at about 1223 K. Oxides of ytterbium and dysprosium were 99.9% pure and were both obtained from Unocal, Molycorp Inc., U.S.A. Holmium oxide and thulium oxide of the same 99.9% purity were obtained from Johnson and Matthey (Germany) Erbium oxide and gadolinium oxide were 99.99% pure and were obtained from Rhone Poulenc (France). Single-crystal CaF_2 pellets used as solid electrolytes were obtained from Gimex (The Netherlands).

The procedure of intermediate grinding, mixing, and pelletizing was repeated three times. Compounds of $\text{Cu}_2\text{Ln}_2\text{O}_5$ type as well as the compound CuGd_2O_4 were prepared in a similar manner from equimolar mixture of CuO and Ln_2O_3 at 1273 K. The electrode pellets were prepared by mixing respective compounds with BaF_2 and then sintering at 1173 K in a stream of dry oxygen. $\text{CaO} + \text{CaF}_2$ reference electrodes were made from equimolar amounts of the components in two steps. First, the pellets were sintered at 1273 K in argon for 24 h, and then after intermediate re-grinding they were sintered again at 1173 K in 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 (9). CaF_2 is a pure ionic conductor and the transport number of the fluoride ion in calcium fluoride is known to be unity. The cell construction in this study followed that used by Alcock and Li (10), and was identical with that used in our previous study (6). The cell assembly used in our work is schematically shown in Fig. 1.

The cell was placed in a horizontal resistance furnace. The temperature was controlled by an Omega CR9700 temperature controller. The experimental temperature was measured with a Pt-PtRh10 thermocouple. Dry, synthetic air (AGA, Sweden), which was virtually water-free, was flowed continuously through the cell vessel. The EMF was measured

with a Keithley 197A electrometer. The equilibrium EMF values were attained in 3 to 10 h depending on temperature. The cell resistance was of order 10 k Ω 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. Once the constant temperature had been reached, the EMF remained constant (± 1 –2 mV) for several hours until the temperature was changed again. Thermal cycling of the cell, under experimental conditions of repeated heating and cooling, produced virtually the same EMF values within recorded scatter of points shown for each cell in Fig. 2. The reversibility of the EMF was also checked by passing the current of 0.1 mA from an external source for 30 s. The EMF returned to the original values within ± 1 mV in about 1–5 minutes depending on the temperature. All features of the cell performance mentioned above speak for the reversible cell behavior, although none of them give undeniable evidence of it. The whole experimental cycle of the cell operation usually took about one week.

3. RESULTS

The following electrochemical cells were assembled:

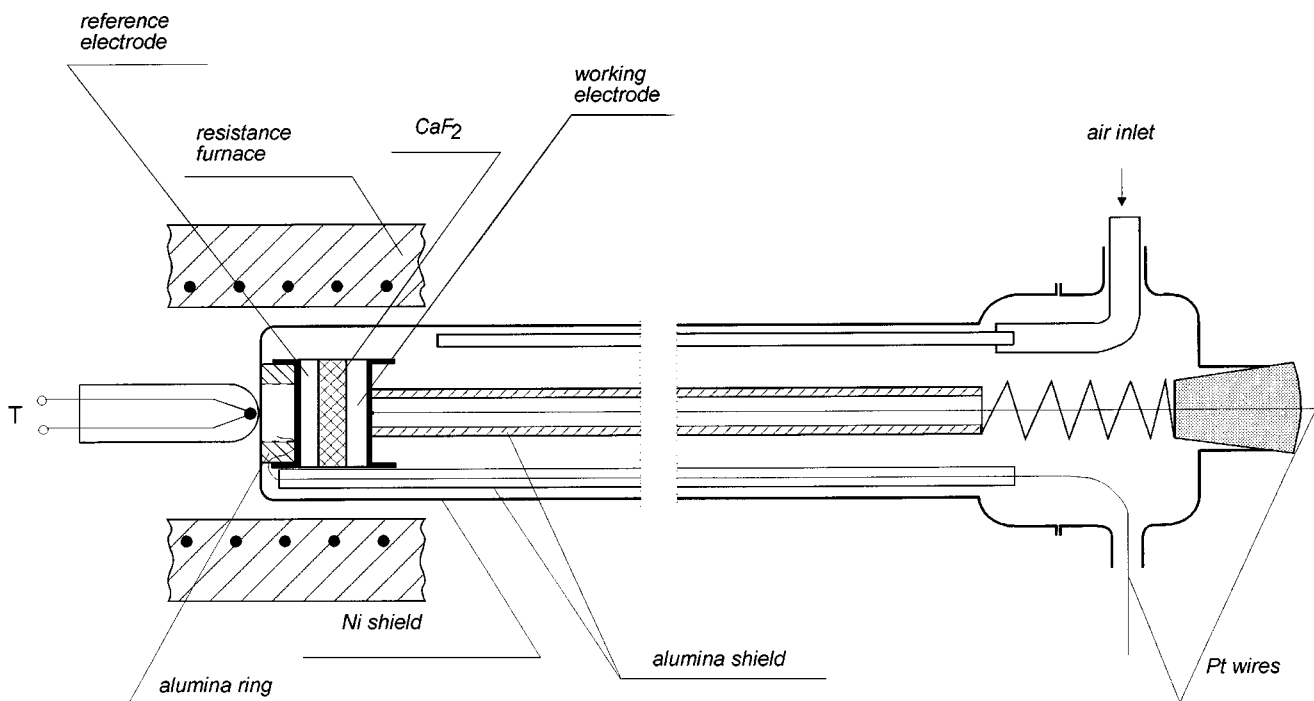
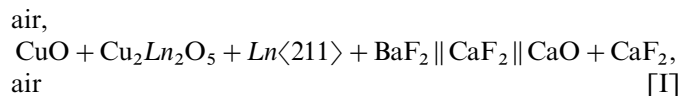


FIG. 1. Schematic diagram of the galvanic cell.

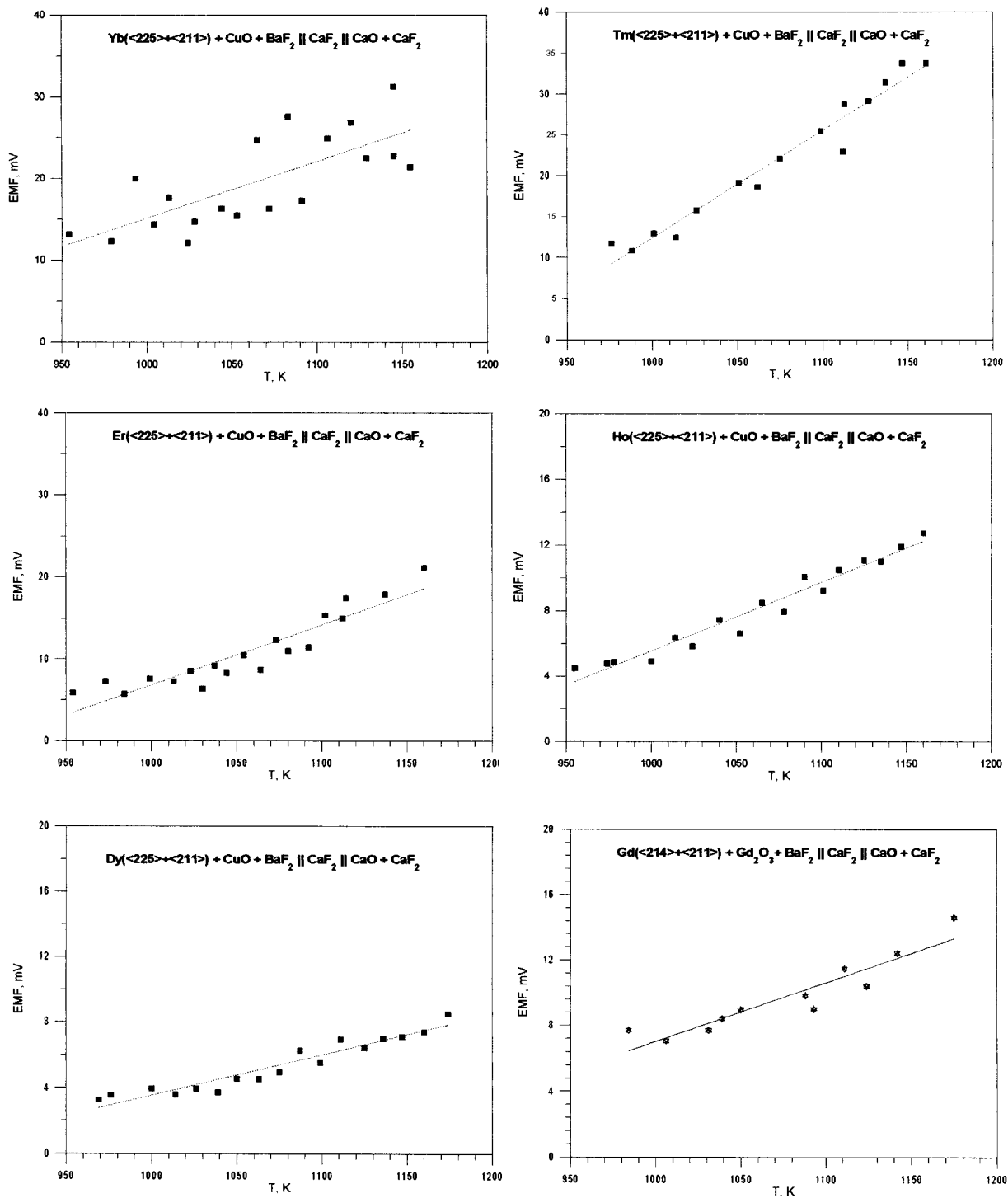


FIG. 2. Variation of EMF with temperature of cells I and II obtained for respective systems.

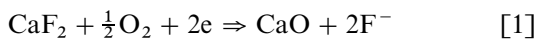
for $Ln = Yb, Tm, Er, Ho, Dy,$ and

air,
 $CuGd_2O_4 + Gd\langle 211 \rangle + Gd_2O_3 + BaF_2 || CaF_2 || CaO + CaF_2,$
 air [II]

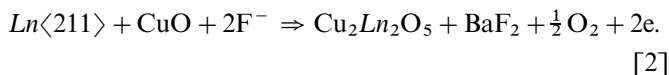
for the Gd compound.

The cells are written in such a way that the right-hand electrodes are positive.

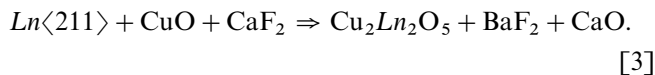
For galvanic cell I the electrode reactions are — at the RHS electrode:



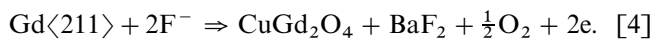
— at the LHS electrode:



Consequently, the net reaction for the cell I is



For galvanic cell II, at the RHS electrode the reaction is identical to reaction [1], while at the LHS electrode the reaction is



The overall cell II reaction is



According to known phase diagrams (7, 11) the mutual solubility between solid phases under considerations is small in the investigated temperature range. Consequently, all components of reactions [3] and [5] are essentially in the pure state. Thus, the Gibbs free energy for spontaneous exchange reactions [3] and [5] may be obtained directly from the measured EMF as

$$\Delta G = -2FE = \sum_i v_i \mu_i = \Delta G^0. \quad [6]$$

It should be mentioned that the change in the Gibbs free energy of the net cell reaction [3]

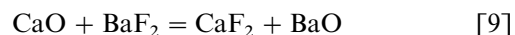
$$\Delta G_{(3)}^0 = -2FE_{\text{I}} \quad [7]$$

is given by the identical expression as the change in the Gibbs free energy of the net cell reaction [5]

$$\Delta G_{(5)}^0 = -2FE_{\text{II}}. \quad [8]$$

The variations of the EMF with temperature determined for investigated systems are shown in Fig. 2. The corresponding linear relations between EMF and temperature are given in Table 1 together with respective ΔG^0 equations, calculated from relations [7] and [8], respectively.

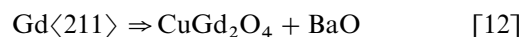
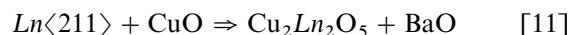
In a previous paper (12) we analyzed the literature data for the exchange reaction



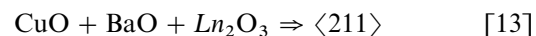
and accepted the change in Gibbs free energy as given by Kaye and Laby (13), which is

$$\Delta G_{(9)}^0(\text{J}) = 63,785 - 3.77 T (\pm 1000) \quad [10]$$

Combining reaction [9] with subsequent reactions [3] and [5] gives the reactions



Finally, using Gibbs free energy change for reactions of formation of respective double oxides from CuO and rare earth oxides (8), one can derive the Gibbs free energy change of the reaction of formation of $\text{Ln}\langle 211 \rangle$ phases from respective oxides:



Consequently, obtained $\Delta G_{\text{oxides}}^0 = f(T)$ equations for $\text{Ln}\langle 211 \rangle$ compounds with subsequent lanthanide elements are also gathered in Table 1.

4. DISCUSSION

The Gibbs free energy change of the reaction of formation of $\text{Ln}_2\text{BaCuO}_5$ phases for $\text{Ln} = \text{Yb}, \text{Tm}, \text{Er}, \text{Ho}, \text{Dy}$, and Gd has been measured in the temperature range 973–1173 K using the EMF technique. As far as we know there are no experimental data in the literature with which our values can be compared. However, our results gathered

TABLE 1
The Observed Electromotive Forces and Respective Gibbs Free Energy Change of the Reaction

Ln	$E_{\text{I or II}} = a + b*T$ (mV)	$\Delta G_{(3) \text{ or } (5)}^0 = A + B*T$ (J/mol)	$\Delta G_{(13)} = A + B*T$ (J/mol)
Yb	$-54.3 + 0.0694*T$ (± 4.0)	$10,490 - 13.40*T$ (± 2350)	$-54,900 - 4.85*T$ (± 2700)
Tm	$-118.8 + 0.1312*T$ (± 2.0)	$22,930 - 6.05*T$ (± 1200)	$-51,500 - 5.00*T$ (± 1800)
Er	$-66.7 + 0.0738*T$ (± 2.0)	$12,860 - 14.18*T$ (± 1200)	$-59,300 - 1.66*T$ (± 1800)
Ho	$-36.3 - 0.0418*T$ (± 1.0)	$7,000 - 8.07*T$ (± 570)	$-52,700 - 7.65*T$ (± 1600)
Dy	$-29.1 + 0.0246*T$ (± 1.0)	$4,070 - 4.75*T$ (± 570)	$-51,200 - 9.06*T$ (± 1600)
Gd	$-29.0 + 0.0360*T$ (± 1.0)	$5,590 - 6.94*T$ (± 570)	$-59,900 - 1.58*T$ (± 1600)

in Table 1 can be partially verified by comparing enthalpy terms with those obtained for Y_2BaCuO_5 and Eu_2BaCuO_5 phases for the reaction of formation from oxides.

As far as Y_2CuBaO_5 is concerned the calorimetric studies of Zhou and Navrotsky (14) Morss *et al.* (15), and Garzon *et al.* (16) gave the following values of the enthalpy of formation from oxides: -59.2 (at 977 K), and -92.0 and -76.2 kJ/mole at room temperature, respectively. These results correspond reasonably well with those derived from EMF studies of Pashin and Tretyakov (17), -61.7 , and Azad *et al.* (18), -72.5 kJ/mole, respectively. Also, determined recently was the enthalpy of formation from oxides value for Eu_2CuBaO_5 (6): -82.5 kJ/mole falls within the similar range. It can be also noticed that enthalpy values derived from $\Delta G_{(13)}^0$ temperature dependence obtained for respective phases (Table 1) are similar. However, the value obtained with the same technique for $Eu\langle 211 \rangle$ is lower. It is not clear at present if this result indicates the dependence of the enthalpy on ionic radius of the lanthanide element. The research is under way to provide similar data for $Sm\langle 211 \rangle$ and $Nd\langle 211 \rangle$ phases in order to extend the range of the possible correlation.

Results gathered in Table 1 also suggest that all $Ln\langle 211 \rangle$ phases are entropy stabilized if the reaction of formation takes place from the constituent oxides.

It should be borne in mind, however, that the split of ΔG^0 equations into enthalpy and entropy terms depends heavily on EMF temperature dependence, and the enthalpy value is sensitive to the slope of that dependence. Moreover, in order to calculate ΔG^0 for reaction [13], the results for reactions

[11] and [12] must be combined with the corresponding equation for ΔG^0 of the reaction of formation of respective double oxides (either $Cu_2Ln_2O_5$ or $CuGd_2O_4$) from oxides (which was determined by us in the previous paper (8)). Consequently, the final result depends on the sum of experimental errors committed at each stage of this procedure. More experimental data, preferably obtained from different techniques, are needed to verify the accuracy of our results.

All cells with lanthanide elements except Gd worked reversibly for about a week yielding reproducible EMF's readings. The behavior of the cell with gadolinium was different. Since in principle only two-phase equilibrium $Gd\langle 211 \rangle-CuGd_2O_4$ assures the establishment of BaO chemical potential in the mixture, we started our experiments with the working electrode $Gd\langle 211 \rangle-CuGd_2O_4-BaF_2$. The change of EMF with temperature recorded for this cell is shown in Fig. 3.

It can be noticed that EMF vs T dependence changed its slope once the highest experimental temperature was reached. X-ray study of the working electrode performed after the experiments showed the formation of the $BaF_2 \cdot GdF_3$ compound. The results of the microprobe analysis suggest that this reaction takes place at the expense of the decomposition of $CuGd_2O_4$ followed by the formation of $GdOF$ as an intermediate compound.

Consequently, we have run more experiments with the following working electrodes:

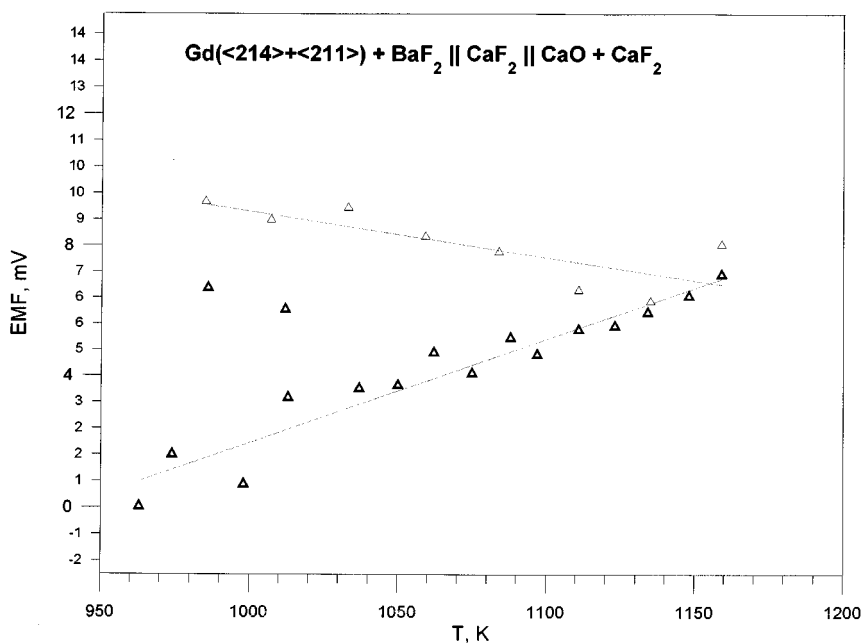
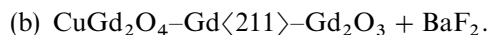
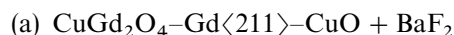


FIG. 3. Variation of EMF with temperature of cell II with $CuGd_2O_4 + Gd\langle 211 \rangle + BaF_2$ working electrode.

In case (a) the side reaction was also observed, although with not so pronounced effects as those observed for the Gd \langle 211 \rangle -CuGd₂O₄-BaF₂ working electrode. In case (b) the side reaction was virtually absent. The results of this cell were accepted for further calculations.

The results obtained in this study created a basis for the determination of the thermodynamic stability of respective lanthanide Ln \langle 123 \rangle compounds for Ln = Yb, Tm, Er, Ho, Dy, and Gd. Since all these Ln \langle 123 \rangle phases remain in equilibrium with CuO and Ln \langle 211 \rangle , respective Gibbs energies for Ln \langle 123 \rangle compounds can now be obtained using the same experimental technique.

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