A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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THERMODYNAMICS OF $GdMnO_3$ AND $GdMn_2O_5$ PHASES DETERMINED BY THE E.M.F. METHOD

WŁASNOŚCI TERMODYNAMICZNE FAZ $GdMnO_3$ I $GdMn_2O_5$ WYZNACZONE METODĄ POMIARU SIŁY ELEKTROMOTORYCZNEJ OGNIWA

Using solid oxide galvanic cells of the type:

$$MnO + Gd_2O_3 + GdMnO_3/O^{-2}/Ni + NiO$$

and

$$Mn_3O_4 + GdMnO_3 + GdMn_2O_5/O^{-2}/\ air$$

the equilibrium oxygen pressure for the following reactions :

$$MnO + 1/2Gd_2O_3 + 1/4O_2 = GdMnO_3$$

$$1/3Mn_3O_4 + GdMnO_3 + 1/3O_2 = GdMn_2O_5$$

was determined in the temperature range from 1073 to 1450 K.
From the determined equilibrium oxygen partial pressure the corresponding G i b b s free energy change for these reactions was derived:

$$\Delta G^0_{f,GdMnO_3}(+/-425J) = -132721(+/-2240) + 51.91(+/-0.81)T$$

$$\Delta G^0_{f,GdMn_2O_5}(+/-670J) = -121858(+/-6176) + 79.52(+/-4.83)T$$

From these data, standard G i b b s energies, enthalpies and entropies of formation of $GdMnO_3$ and $GdMn_2O_5$ from component oxides and from the elements are derived. Thermodynamic data tables for the two ternary phases are compiled from 298.15 to 1400 K.

W pracy przedstawiono wyniki badań dotyczące stabilności termodynamicznej manganianów gadolinu $GdMnO_3$ i $GdMn_2O_5$ wyznaczonej metodą pomiaru SEM następujących ogniw:

$$MnO + Gd_2O_3 + GdMnO_3/O^{-2}/Ni + NiO$$

i

$$Mn_3O_4 + GdMnO_3 + GdMn_2O_5/O^{-2}/\ air$$

określając jednocześnie równowagowe, parcjalne ciśnienie tlenu dla reakcji:

$$MnO + 1/2Gd_2O_3 + 1/4O_2 = GdMnO_3$$

$$1/3Mn_3O_4 + GdMnO_3 + 1/3O_2 = GdMn_2O_5$$

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Na bazie tych danych określono zależności temperaturowe energii swobodnej G i b b s a, entalpii i entropii tworzenia faz $GdMnO_3$ i $GdMn_2O_5$ zarówno z odpowiednich tlenków jak i pierwiastków w zakresie temperatur 1073–1450K.

$$\Delta G^0_{f,GdMnO_3}(+/-425J) = -132721(+/-2240) + 51.91(+/-0.81)T$$

$$\Delta G^0_{f,GdMn_2O_5}(+/-670J) = -121858(+/-6176) + 79.52(+/-4.83)T$$

Dane termodynamiczne dla dwóch potrójnych faz zamieszczono w tablicach rozszerzając je na zakres 298–1400K.

1. Introduction

Richness of physical phenomena which is displayed by rare-earth manganites stimulated intensive research on these interesting materials. Especially, so-called giant magneto-resistance (GMR), characteristic for the phases with perovskite structure with general stoichiometry *Ln*MnO_3, attracted considerable attention. Phases of *Ln*MnO_3 type were obtained for all rare-earth elements. They exist in two types of structural modifications: orthorhombic for elements from La to Dy, and hexagonal for elements from Ho to Lu, based on the ilmenite type structure [1,2]. The hexagonal structure under high pressure of 4.2–4.5 GPa, and at elevated temperatures 950–1123 K, can be transformed into perovskite — type structure [3].

Since thermodynamic data for these ternary oxides are needed to optimize synthesis and fabrication processes it is not surprising that attempts have been made to enlarge this kind of information. Recently, phase equilibria were established in the Gd — Mn — O system at 1373K by K i t a y a m a *et al.* [4]. They presented the phase diagram which shows that two ternary phases $GdMnO_3$ and $GdMn_2O_5$ are present in this system. However, standard G i b b s energy changes for respective reactions of formations are given in this work only at constant temperature 1373 K. Literature survey revealed that there are only two other studies which report thermodynamic data for these phases. A t s u m i *at al* [5] determined standard G i b b s free energy of formation of $GdMnO_3$ by means of the e.m.f. method using stabilized zirconia as a solid electrolyte. In turn, S a t o h *et al* [6] determined decomposition oxygen partial pressure of $GdMn_2O_5$ as a function of temperature using thermogravimetry and differential thermal analysis. In the present paper an attempt has been made to provide new thermodynamic data derived from the same experimental technique we used in our previous investigations [7-9]. Electrochemical cells with zirconia solid electrolyte were used to determined Gibbs free energy of formation of $GdMnO_3$ and $GdMn_2O_5$ phases existing in ternary Gd-Mn-O system. Then, a consistent set of thermodynamic data for these two phases has been compiled from 298.15 to 1400 K.

2. Experimental

Materials

Pure oxides of Gd_2O_3 (99.9% — Unocal, Molycorp Inc.USA), MnO (99.9%), Mn_2O_3 and Mn_3O_4 (prepared by heating of MnO_2 under proper conditions) were used as starting materials to prepare respective phases. Gd_2O_3 was dried in air at 1273K for 24 hours and Mn_2O_3 was calcined in air at 1023K. Next, an equimolar mixture of Gd_2O_3 and Mn_2O_3 was prepared, pressed into pellets and fired at 1550 K in argon atmosphere for 72 hours. The pellets were reground in an agate mortar under acetone, pressed once more and heated at 1273 K for 48 hours . Phase identification was made by XRD analysis (Philips type PW 1710) which showed that the obtained material consisted of $GdMnO_3$ phase and only traces of Gd_2O_3 oxide were present in it.

The high purity argon gas 99.998% (AGA gas — 4.8) was used to provide an inert gas atmosphere for the synthesis of electrodes. It was additionally deoxidized by passing through copper shavings at 723 K and then through silica gel and anhydrous $Mg(ClO_4)_2$.

We tried to obtain another compound, $GdMn_2O_5$, using previously prepared $GdMnO_3$, Mn_2O_3 and Mn_3O_4 as substrates. The equimolar mixtures of GdMnO3-Mn_2O_3 and GdMnO3-Mn_3O_4 in the form of pressed pellets were placed in the platinum boat inside the quartz tube. The samples were heated at 1223 K for 132 hours in pure oxygen flowing through the system. Then, the samples were cooled quickly by pulling out the Pt boat into furnace cold zone which was cooled by the water jacket. The X-ray powder analysis showed that $GdMn_2O_5$ was the main product of the reaction; in the samples we found also small amounts of Mn_3O_4 and $GdMnO_3$. We used this product of the synthesis, after the addition of $GdMnO_3$ and Mn_3O_4 as the working electrode ready for the EMF experiment.

Technique

Two types of e.m.f. cells were used in our experiments and they are shown in Figures 1 and 2. The first cell I (Fig. 1) was applied to the EMF measurements with $GdMnO_3$ + Gd2O_3 + MnO phases mixture as the working electrode, and the second one was used to determine the EMF produced by the $GdMn_2O_5$ + $GdMnO_3$ + Mn_3O_4 working electrode (Fig. 2).

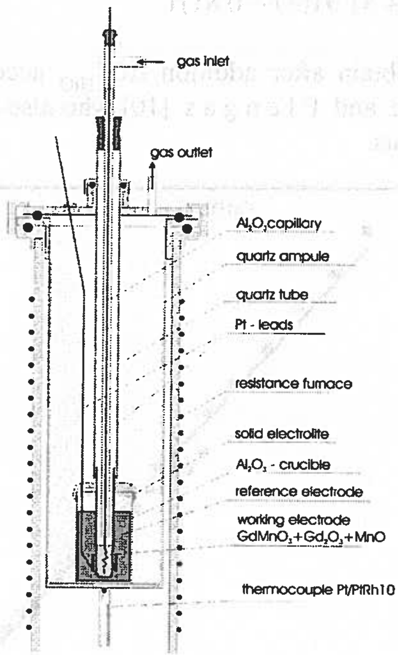

Fig. 1. Schematic diagram of the apparatus used for the EMF measurements of cell I

In the first case the reference electrode was the mixture of Ni+NiO in molar ratio 1.5 : 1. The investigated electrode contained the mixture of the phases with the molar ratio 2 : 2.5 : 1 respectively. The working electrode and reference electrode were placed in a crucible made of alumina, sealed with high temperature cement and placed in closed one end quartz tube. Before the experiment the whole system was flushed with pure argon. Then, the temperature was raised and the cell was working under argon atmosphere. The temperature of the furnace was controlled by Eurotherm temperature controller and EMF was measured with high resistance multimeter Keithley 2000. The course of the experiment (EMF vs. time necessary to reach the equilibrium by the system) was recorded by a computer. The cell was working for about 2 weeks and the measurements were taken at increasing and decreasing temperature.
In the second case the reference electrode was the air that was flushing from outside a long tube of the solid electrolyte (Fig. 2). The working electrode consisted of a mixture of $GdMn_2O_5$, $GdMnO_3$ and Mn_3O_4, and it was placed inside the electrolyte tube. Before the experiment the tube was flushed with argon and then the flow of argon was maintained during measurements. The EMF measurements were taken in the same way as described before for the cell I. The whole experimental run took about two weeks.

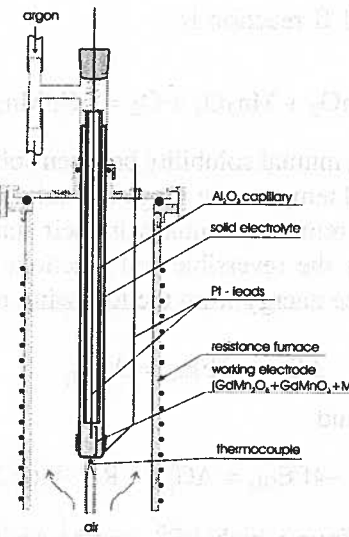

Fig. 2. Schematic diagram of the apparatus used for the EMF measurements of cell II

Principles

The following electrochemical cells were assembled:

$$MnO + Gd_2O_3 + GdMnO_3|O^{-2}|Ni + NiO, \qquad \mathbf{I}$$

and

$$Mn_3O_4 + GdMnO_3 + GdMn_2O_5|O^{-2}|air \qquad \mathbf{II}$$

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

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

$$NiO + 2e = Ni + O^{-2} \qquad (1)$$

-at the LHS electrode:

$$O^{-2} + 2MnO + Gd2O3 = 2GdMnO_3 + 2e \qquad (2)$$

Consequently, the net cell reaction for the cell I is:

$$NiO + 2MnO + Gd_2O_3 = Ni + 2GdMnO_3 \qquad (3)$$

from which, after the addition of the reaction of formation of NiO from pure elements , the reaction of formation of $GdMnO_3$:

$$2MnO + 1/2O_2 + Gd_2O_3 = 2GdMnO_3 \qquad (4)$$

is obtained.

For galvanic cell II, at the RHS electrode the following reaction takes place:

$$O_2 + 4e = 2O^{-2} \qquad (5)$$

while at the LHS electrode the reaction is:

$$2O^{-2} + Mn_3O_4 + 3GdMnO_3 = 3GdMn_2O_5 + 4e \qquad (6)$$

The overall cell II reaction is:

$$3GdMnO_3 + Mn_3O_4 + O_2 = 3GdMn_2O_5 \quad (7)$$

Neglecting mutual solubility between solid phases in the investigated temperature range (all solid components of the reaction remain essentially in their standard state) one obtains for the reversible cell reactions the change in G i b b s free energy from the following relationship:

$$\Delta G = -2FE_{(I)} = \Delta G^0_{(3)} \quad (8)$$

for the cell I, and

$$\Delta G = -4FE_{(II)} = \Delta G^0_{(6)} - RT \cdot \ln(0.21) \quad (9)$$

for the cell II, from which $\Delta G^0_{(6)}$ can be easily obtained:

$$\Delta G^0_{(6)} = -4FE_{(II)} + RT \cdot \ln(0.21) \quad (10)$$

The variations of the EMF's with temperature determined for the investigated systems are shown in Figures 3 and 4. Both cells produced reproducible EMF values for more than one week. The corresponding linear relations between EMF and temperature were obtained by the least-squares fit, and they have the following form:

$$E_I(+/-1.9mV) = 164.7(+/-5.2)- \\ -0.09808(+/-0.004)T \quad (11)$$

$$E_{II}(+/-5.4mV) = 947.0(+/-16)- \\ -0.652(+/-0.013)T \quad (12)$$

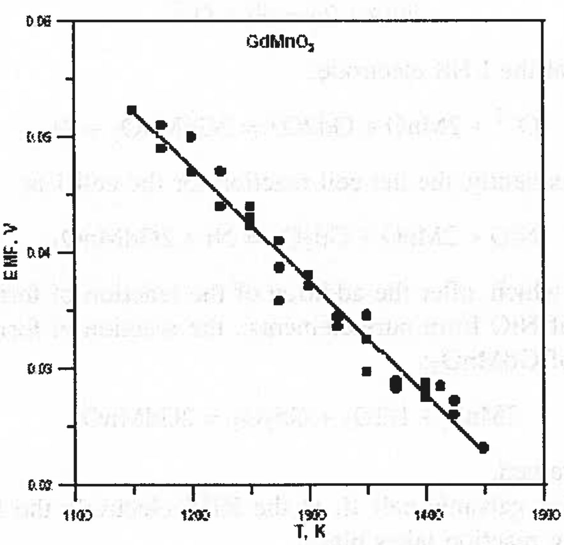

Fig. 3. Fig. 3. The EMF vs. T plot for cell I

Respective ΔG^0 changes for reaction (3) and (7) were calculated from our EMF data, and they are as follows:

$$MnO + 1/4O_2 + 1/2Gd_2O_3 = GdMnO_3 \quad (13)$$

in the form:

$$\Delta G^0_{(13)}(+/-425J) = -132721(+/-2240)+ \\ +51.91(+/-0.81)T \quad (14)$$

which we obtain after addition $\Delta G^0_{f,NiO}$ accepted after C h a r e t t e and F l e n g a s [10] who also used EMF measurements.

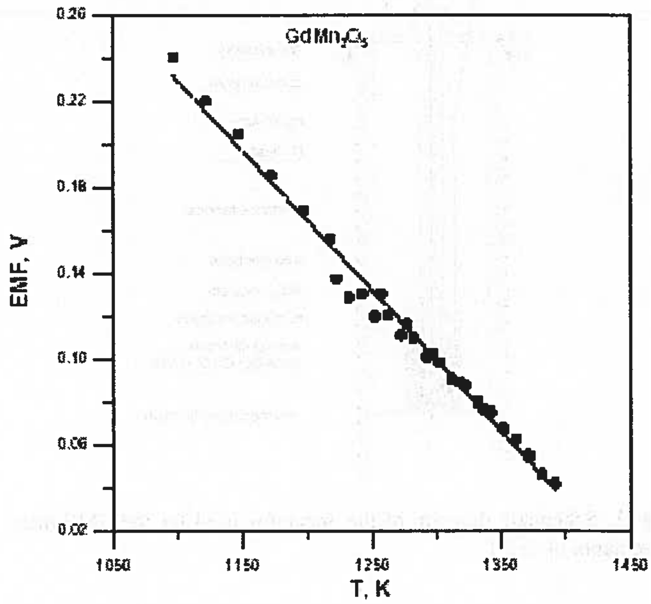

Fig. 4. The EMF vs. T plot for cell II+

In turn, for the reaction:

$$GdMnO_3 + 1/3Mn_3O_4 + 1/3O_2 = GdMn_2O_5 \quad (15)$$

respective G i b b s free energy change per one mole of the phase is:

$$\Delta G^0_{(15)}(+/-670J) = -121858(+/-6176)+ \\ +79.52(+/-4.83)T \quad (16)$$

which was obtained directly from eq.9 assuming $p_{O_2} = 0.21$ atm at the air reference electrode.

3. Standard enthalpies of formation and standard entropies of formation of $GdMnO_3$ and $GdMn_2O_5$

Having given eqs. 14 and 16, the G i b b s free energy of formation of $GdMnO_3$ and $GdMn_2O_5$ from oxides can be derived in the following manner. From the data of R o b i e and H e m i n g w a y [11] the change in standard G i b b s energy for the oxidation of MnO to Mn_2O_3 reaction:

$$MnO + {}^1/_4O_2 \Rightarrow Mn_2O_3 \quad (17)$$

in the considered temperature range is:

$$\Delta G^0_{(17)} = -91748 + 51.12T(J/mol) \quad (18)$$

with the uncertainty ± 195 J / mol. Coupling two reactions (13) and (17), the Gibbs energy of formation of $GdMnO_3$ from its component oxides:

$$^1/_2Gd_2O_3 + ^1/_2Mn_2O_3 \Rightarrow GdMnO_3 \quad (19)$$

is given by:

$$\Delta G^0_{(19)} = -40973(+/-3000) + 0.79 \\ (+/-0.83)T\ (J/mole) \quad (20)$$

with the uncertainty estimated as +/- 470 J.

The temperature independent term in the last equation (20) represents the enthalpy of formation of $GdMnO_3$ phase from respective oxides at the mean experimental temperature 1300 K. Temperature dependent term is related to corresponding entropy change for reaction of $GdMnO_3$ formation from oxides at the same temperature. Assuming that Kopp-Neumann rule is valid, the resulting Δc_p for the solid state reaction is zero, and ΔH^0 is independent on temperature. Consequently, ΔH^0_{298} is obtained as - 40.97 (+/- 3) kJ/mol, and corresponding standard entropy change is - 0.79 (+/- 0.83) J/mol K at 298 K.

The enthalpy of formation of $GdMnO_3$ from its elements Gd, Mn and O_2 at 298 K can be obtained from evaluated above enthalpy change and the enthalpies of Gd_2O_3 and Mn_2O_3 given in compilation of Pankratz [12] and Robie and Hemingway [11]. Its calculated value is equal to -1433.91 kJ/mol (+/- 3.53). The standard entropy of $GdMnO_3$ at 298 K evaluated in the similar manner is 129.75 J/mol K (+/- 0.94).

Similarly, the Gibbs energy of formation of $GdMn_2O_5$ from binary oxides Gd_2O_3, Mn_2O_3 and MnO_2 due to reaction:

$$1/2Gd_2O_3 + 1/2Mn_2O_3 + MnO_2 \Rightarrow GdMn_2O_5 \quad (21)$$

can be evaluated in the following way.

Having the Gibbs energy of formation of $GdMn_2O_5$ from $GdMnO_3$, Mn_3O_4 and O_2 according to reaction (15) and accepting standard Gibbs energy change recalculated in the previous study [7] for the reaction of Mn_3O_4 oxidation:

$$1/3Mn_3O_4 + 1/3O_2 \Rightarrow MnO_2 \quad (22)$$

for which:

$$\Delta G^0_{(22)} = -57329 + 68.43T(+/-800J) \quad (23)$$

and combining reactions (15), (22) and (19), the Gibbs free energy of formation of $GdMn_2O_5$ from oxides Gd_2O_3, Mn_2O_3 and MnO_2 according to reaction (21) is obtained as:

$$\Delta G^0_{(21)} = -105502(+/-3880) + 11.88 \\ (+/-1.82)TJ/mol \quad (24)$$

with the uncertainty of +/- 1145 J/mol.

Applying the Kopp–Neumann rule to the reaction (19), the values of $\Delta H^0_{298} = -105.5(+/-3.9)$ kJ/mol and $\Delta S^0_{298} = -11.88(+/-1.82)$ J/mol K are obtained. The enthalpy of formation of $GdMn_2O_5$ from its elements Gd, Mn, and O_2 at 298.15 K is - 2018.44 (+/-4.27) kJ/mol. The standard entropy of $GdMn_2O_5$ at 298.15 K is 171.41 (+/-1.92) J/mol K. Corresponding thermodynamic data for Gd_2O_3 were taken again after Pankratz [12], while those for Mn_2O_3 and MnO_2 from Robie and Hemingway's paper [11].

4. Thermodynamic Data Tables for $GdMnO_3$ and $GdMn_2O_5$ from 298.15 to 1400 K

Thermodynamic data tables for $GdMnO_3$ and $GdMn_2O_5$ can be derived from the information obtained in this study and from literature data. The results are summarized in Tables 1 and 2. Values for $\{H^0(T) - H^0(298.15)\}$, $S^0(T)$ and $\{S^0(T) - S^0(298.15)\}$ for both compounds have been evaluated based on the assumption that the heat capacity of the ternary oxides follows Kopp-Neumann rule. The values of the Gibbs free energy function (fef) are evaluated from component terms as $(G^0_T - H^0_T)/T = -S^0_T + (H^0_T - H^0_{298.15})/T$. The enthalpy of formation of $GdMnO_3$ and $GdMn_2O_5$ from the elements at each temperature is evaluated using the data assessed in this study for the two compounds and values for Gd, Mn and O_2 from Pankratz [12]. Values for the Gibbs free energy of formation of $GdMnO_3$ and $GdMn_2O_5$ from elements are obtained at regular intervals of temperature using the relation $\Delta G^0_f = \Delta H^0_f - T\Delta S^0_f$. Of course, these data can be further refined when both low-temperature and high-temperature experimental heat capacity data become available for these ternary oxides.

TABLE 1

$GdMnO_3$

T/K	C_p J/mol K	S^o J/mol K	$H^o_T-H^o_{298}$ kJ/mol	$S^o_T-S_{298}$ J/mol K	fe f J/mol K	ΔH^o_f kJ/mol	ΔG^o_f kJ/mol
298.15	103.63	129.75	0	0	-129.75	-1433.91	-1351.21
400	111.53	161.44	11.001	31.693	-133.94	-1433.66	-1322.97
500	116.99	186.94	22.440	57.195	-142.06	-1432.71	-1295.39
600	121.32	208.67	34.362	78.920	-151.40	-1431.14	-1268.05
700	124.98	227.65	46.681	97.903	-160.96	-1430.02	-1240.93
800	128.22	244.55	59.344	114.807	-170.38	-1428.58	-1214.02
900	131.18	259.83	72.316	130.082	-179.48	-1427.16	-1187.28
1000	133.95	273.80	85.574	144.049	-188.22	-1428.04	-1160.66
1100	136.58	286.68	99.102	156.941	-196.59	-1426.72	-1133.98
1200	139.11	298.68	112.887	168.934	-204.61	-1425.42	-1107.43
1300	141.57	309.92	126.922	180.167	-212.28	-1424.14	-1080.98
1400	143.98	320.49	141.199	190.746	-219.64	-1424.46	-1053.85

TABLE 2

$GdMn_2O_5$

T/K	C_p J/mol K	S^o J/mol K	$H^o_T-H^o_{298}$ kJ/mol	$S^o_T-S_{298}$ J/mol K	fe f J/mol K	ΔH^o_f kJ/mol	ΔG^o_f kJ/mol
298.15	158.41	171.41	0	0	-171.41	-2018.44	-1877.55
400	174.75	220.49	17.047	49.081	-177.87	-2013.79	-1830.07
500	185.34	260.70	35.086	89.294	-190.53	-2006.94	-1784.89
600	192.53	295.17	54.001	123.761	-205.17	-1998.44	-1741.25
700	197.66	325.25	73.522	153.846	-220.22	-1988.63	-1699.15
800	201.57	351.91	93.488	180.506	-235.05	-1977.70	-1658.53
900	204.83	375.85	113.809	204.440	-249.39	-1965.76	-1619.35
1000	207.81	397.59	134.438	226.176	-263.15	-1955.10	-1581.49
1100	210.78	417.53	155.361	246.121	-276.29	-1941.79	-1544.81
1200	213.92	436.00	176.589	264.595	-288.85	-1926.12	-1509.43
1300	217.39	453.26	198.144	281.852	-300.84	-1909.91	-1475.34
1400	221.29	469.51	220.066	298.103	-312.32	-1890.17	-1438.37

5. Discussion

The thermodynamic stability of $GdMnO_3$ and $GdMn_2O_5$ phases was determined from EMF measurements which were carried out in the temperature range from 1050 to 1450 K. Galvanic cells with solid oxide zirconia electrolyte were used to determine equilibrium oxygen partial pressure as a function of temperature for respective three-phase equilibria. These cells worked reversibly over a period of about two weeks. Reversibility was confirmed by recording of repeatable EMF's during temperature cycling as well as EMF's. return to the previous value after the disturbance of the cell with small current passed through it. No sign of side reactions was observed during the cell operation. Examination of used Pt wire after experiments (which was in contact with the working electrode) did not show signs of Mn transfer from the electrode into the metal. Separate experiments with Gd_2O_3 pellet in contact at 1323 K with the zirconia electrolyte did not show signs of exchange reaction between oxides. Microprobe (Philips type XL30 with EDS INK ISIS) analysis did not show the presence of Gd in the electrolyte. Thus one may assume that side reactions are negligible in the cell, at least up to 1400 K.

Obtained Gibbs free energy changes for reactions of formation of $GdMnO_3$ and $GdMn_2O_5$ are shown and compared with the results of the study of Atsumi *et al* [5] and Satoh *et al* [6] in Figures 5 and 6. It is seen that the results of Atsumi et al are almost identical with the results of this study, differing slightly from our temperature dependence. Atsumi *et al* [5] used also EMF technique. They used Fe + FeO reference electrode and consequently their cells had to produce higher EMF's than those measured in this study. Such a choice of the reference electrode does not always mean higher precision of EMF measurements.

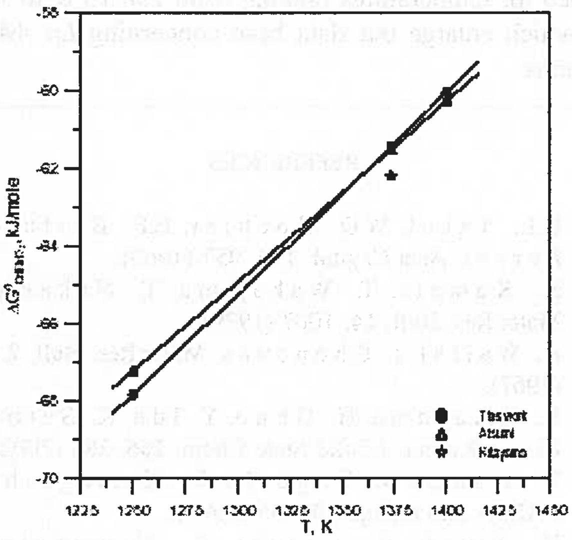

Fig. 5. Comparison of the G i b b s energy change of $GdMnO_3$ formation vs. temperature obtained in this work with data reported in literature

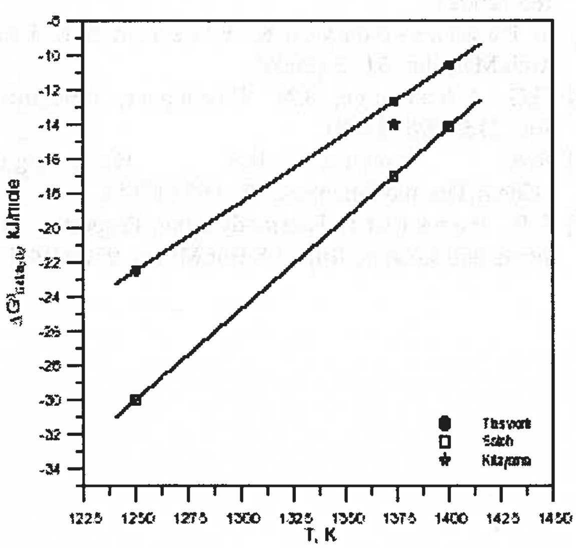

Fig. 6. The plot of the G i b b s energy change of $GdMn_2O_5$ formation vs. temperature in the range 1200 - 1400K

Unfortunately, in their paper neither graphs nor equations of the EMF plots vs. temperature are given. Therefore, it is difficult to assess accuracy of their cell performance. In turn S a t o h *et al* [6] applied thermogravimetry and differential thermal analysis under various oxygen partial pressures to determine decomposition temperature of respective $LnMn_2O_5$ phases. From the oxygen partial pressure at the decomposition temperature G i b b s free energy of decomposition reactions was determined. Since the applied method is a dynamic one, the true equilibrium is rather difficult to achieve in the system, even with slow heating rate. This is especially inconvenient under low oxygen partial pressure (i.e. at lower temperature) when diffusion slows down. Consequently, reversibility of the decomposition reaction is difficult to achieve. That's probably why they results differ more at lower experimental temperature. In the recent study of K i t a y a m a *et al* [4] G i b b s free energy change for respective reactions is given only at one temperature 1373 K. These values are also shown in the Figures 5 and 6 and one can observe that they are about 1 kJ lower than our values, while they also differ significantly from those of S a t o h *et al* in the case of $GdMn_2O_5$ phase.

Using the results of this study the oxygen potential diagram for the system Gd–Mn–O was derived at the temperature 1373 K and is shown in Fig. 7. The composition variable z is the molar fraction $n_{Mn}/(n_{Mn} + n_{Gd})$. Calculated lines are compared with the results of the recent study of K i t a y a m a *et al* [4] who established phase equilibrium in the system Mn-Gd-O at 1373 K while varying the partial pressure of oxygen between 0 and 13.0 in -log (p_{O2}/atm). Equilibrium lines given in [4] are shown in Fig. 7 with dotted lines.

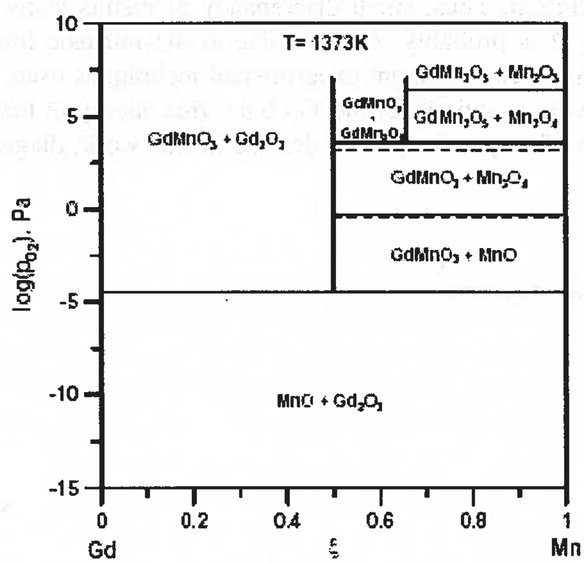

Fig. 7. Oxygen potential diagram of the Gd - Mn - O system at constant temperature 1373K; dotted lines - K.Kitayama et al. **[4]**

It is seen that while the results are almost identical at low oxygen potential (reaction 13), for high oxygen potential (reaction 15) they differ slightly. This small difference can be attributed to different experimental techniques used in our and their studies. We do not think it results from the nonstoichiometry of the $GdMnO_3$ phase. K i t a y a m a *et al* [4] reported the range of nonstoichiometry of the $GdMnO_3$ phase coexisting with Gd_2O_3. According to their study x in $GdMnO_{3+x}$ ranges from - 0.03 at log $p_{O2} = -9.47$ to + 0.05 at log $p_{O2} = 0$. They also showed that x almost does not vary in the range of oxygen pressures from log $p_{O2} = -4.0$ to log $p_{O2} = -9.47$, and corresponds to oxygen deficient phase of approximately constant composition $GdMnO_{2.97}$ Thus, very good agreement between this study and K i t a y a m a *et al* achieved at low oxygen potential is not surprising. It means that results of our measurements correspond rather to oxygen deficient phase since log p_{O2} measured by our cell I varied in the investigated temperature range between -8.3 and -13.3. In this p_{O2} range the composition of the phase remained practically constant.

There is a question however if it results in slight discrepancy of log p_{O2} obtained at high oxygen potentials for reaction (15). At these pressures $GdMnO_{3+x}$ phase is no longer oxygen deficient but its oxygen content may vary from 2.98 to 3.01 in the investigated temperature range. However, this fact should not have influence on the discrepancy shown in Fig. 7. Since oxygen partial pressure was measured directly by EMF over the three-phase field it had to correspond to real composition of the $GdMnO_3$ phase provided equilibration was fast enough to produce its equilibrium composition. We assumed that at high oxygen potentials it happened due to long time of cell operation. Thus, small discrepancy of results shown in Fig. 7 is probably observed due to the intrinsic limitations of two different experimental techniques used.

Having equations for the G i b b s free energy of formation of respective phases derived in this work, diagrams as that shown in Fig. 7 can be easily calculated under different conditions imposed by the choice of T and p_{O2} variables. This may help to establish proper conditions for the preparation of the chosen compound. Also, thermodynamic data tables for the two oxides are presented for temperatures ranging from 298.15 K to 1400 K, which enlarge our data base concerning *Ln* -Mn-O systems.

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REFERENCES

[1] H.L. Y a k e l, W.D. K o e h l e r, E.F. B e r t a u t, F. F o r r o t, Acta Crystal. **116**, 957 (1963).

[2] K. K a m a t a, T. W a k a j i m a, T. N a k a m u r a, Mater.Res. Bull. **14**, 1007 (1979) .

[3] A. W a i t a l, J. C h e n o v a s, Mater.Res. Bull. **2**, 819 (1967).

[4] K. K i t a y a m a, H. O h n o, Y. I d e, K. S a t o h, S. M u r a k a m i, J.Solid State Chem. **166**, 285 (2002).

[5] T. A t s u m i, T. O h g u s h i, N. K a m e g a s h i r a, J.Alloys and Comp. **238**, 35 (1996).

[6] H. S a t o h, S. S u z u k i, K. Y a m a n o t o, N. K a m e g a s h i r a, J.Alloys and Comp. **239**, 1 (1996).

[7] K.T. J a c o b, Mrinalini Attaluri, K.Fitzner Calphad, **26**, 313 (2002).

[8] E. P a w l a s - F o r y s t, K. F i t z n e r, Arch.Met. **47**, 385 (2002).

[9] E. P a w l a s - F o r y s t, K. F i t z n e r, K.T. J a c o b, Arch.Met.Mat. **51**, 2 (2006).

[10] G.G. C h a r e t t e, S.N. F l e n g a s, J.Electrochem. Soc. **115**, 796 (1968).

[11] R.A. R o b i e, B.S. H e m i n g w a y, J.Chem.Thermodynamics, **17**, 165 (1985).

[12] L.B. P a n k r a t z, Thermodynamic Properties of Elements and Oxides, Bull.U.S.Bur.Mines, 972 (1982).