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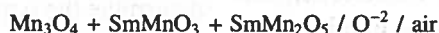
THERMODYNAMICS OF SmMnO3 AND SmMn2O5 PHASES DETERMINED BY THE E.M.F. METHOD

## STABILNOŚĆ TERMODYNAMICZNA FAZ SmMnO3 I SmMn2O5 WYZNACZONA METODĄ POMIARU SIŁY ELEKTROMOTORYCZNEJ OGNIWA

Using solid oxide galvanic cells of the type:

$$MnO + Sm_2O_3 + SmMnO_3 / O^{-2}/ Ni + NiO$$

and

$$Mn_3O_4 + SmMnO_3 + SmMn_2O_5 / O^{-2} / air$$

the equilibrium oxygen pressure for three-phase equilibria described by the following reactions of formation of ternary phases:

$$MnO + 1/2Sm_2O_3 + 1/4O_2 = SmMnO_3$$

$$1/3Mn_3O_4 + SmMnO_3 + 1/3O_2 = SmMn_2O_5$$
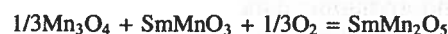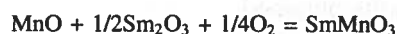
was determined in the temperature range from 1173 to 1450 K. From the obtained experimental data the corresponding Gibbs free energy change for above reactions of phases formation was derived:

$$\Delta G^0_{f,SmMnO3}(+/-250J) = -131321(+/-2000) + 48.02(+/-0.35)T / K$$

$$\Delta G^0_{f,SmMn2O5}(+/-2000\,J) = -107085(+/-2200) + 69.74(+/-1.70)T / K$$

Using obtained results and available literature data, thermodynamic data tables for the two ternary phases have been compiled from 298.15 to 1400 K.

W pracy przedstawiono wyniki badań dotyczące własności termodynamicznych manganinów samaru, wyznaczone metodą pomiaru SEM ogniw ze stałym elektrolitem:
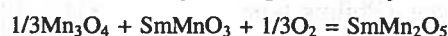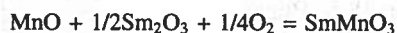
$$MnO + Sm_2O_3 + SmMnO_3 / O^{-2}/ Ni + NiO$$ ogniwo I

$$Mn_3O_4 + SmMnO_3 + SmMn_2O_5 / O^{-2} / powietrze$$ ogniwo II

oraz określono równowagowe ciśnienie parcjalne tlenu dla reakcji tworzenia SmMnO3 i SmMn2O5 w zakresie temperatur 1173–1450 K:

$$MnO + 1/2Sm_2O_3 + 1/4O_2 = SmMnO_3$$

$$1/3Mn_3O_4 + SmMnO_3 + 1/3O_2 = SmMn_2O_5$$

Z tych danych doświadczalnych wyznaczono zależności temperaturowe energii swobodnych tworzenia powyższych manganinów samaru:

$$\Delta G^0_{f,SmMnO3}(+/-250J) = -131321(+/-2000) + 48.02(+/-0.35)T / K$$

$$\Delta G^0_{f,SmMn2O5}(+/-2000\,J) = -107085(+/-2200) + 69.74(+/-1.70)T / K$$

W tablicach I i II zamieszczono dane termodynamiczne dla dwóch potrójnych faz otrzymane poprzez kompilację własnych danych doświadczalnych z danymi literaturowymi.

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1. Introduction

It is known that in the ternary Ln-Mn-O systems (Ln = lanthanide element) three types of oxide phases, namely $LnMnO_3$, $LnMn_2O_5$ and Ln_2MnO_4 may exist [1]. Among them the phase $LnMnO_3$ – type is of special interest. It is formed with all lanthanide elements and, depending on the conditions, may exhibit perovskite structure. It is this type of the phase, in which the so-called magnetoresistance effect may take place. This phenomenon makes these materials very attractive for electronic industry. Therefore, it is not surprising that the determination of conditions necessary to optimize phase's synthesis and fabrication processes became important.

In the previous paper we investigated thermodynamic stability of respective phases in Nd-Mn-O system [2, 3]. In the present paper an attempt has been made to provide thermodynamic data for Sm-Mn-O system using the same experimental technique Electrochemical cells with zirconia solid electrolyte were employed to determine Gibbs free energy of formation of $SmMnO_3$ and $SmMn_2O_5$ phases. Then, using the results obtained in this work, 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 Sm_2O_3 (99.999% from Johnson Matthey Co.), MnO (99.9%), Mn_2O_3 (99% from Aldrich) and Mn_3O_4 (prepared by heating of Mn_2O_3 under proper conditions) were used as starting materials to prepare respective phases. Sm_2O_3 was dried in air at 1123K for 26 hours. Mn_2O_3 was calcined in air at 1023K for 70 hours. Next, an equimolar mixture of Sm_2O_3 and Mn_2O_3 was prepared, pressed into pellets under 8000kG and fired at 1560K in air atmosphere for 72 hours. The pellets were reground in an agate mortar under acetone, pressed once more and heated at 1273 K for 48 h. Phase identification was made by XRD analysis (Philips type PW 1710) It showed that the obtained material consisted of $SmMnO_3$ phase and only traces of Sm_2O_3 were present in it.

High purity argon gas 99.998% (AGA gas – 4.8) was used to provide an inert gas atmosphere for the synthesis of electrodes, and 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 $SmMn_2O_5$ using previously prepared $SmMnO_3$, Mn_2O_3 and Mn_3O_4 as substrates. The equimolar mixtures of $SmMnO_3$-Mn_2O_3 and $SmMnO_3$-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 $SmMn_2O_5$ was the main product of the reaction; in the samples we found also small amounts of Mn_3O_4 and $SmMnO_3$. We used this product of the synthesis, after the addition of $SmMnO_3$ 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 e.m.f measurements with the mixture of $SmMnO_3$+ Sm_2O_3+ MnO phases as the working electrode, and the second one was used to determine the e.m.f. produced by the cell with $SmMn_2O_5$ + $SmMnO_3$ + Mn_3O_4 working electrode (Fig. 2).

gas inlet

gas outlet

Al_2O_3 capillary

quartz ampule

quartz tube

Pt - leads

resistance furnace

solid electrolite

Al_2O_3 - crucible

reference electrode

working electrode
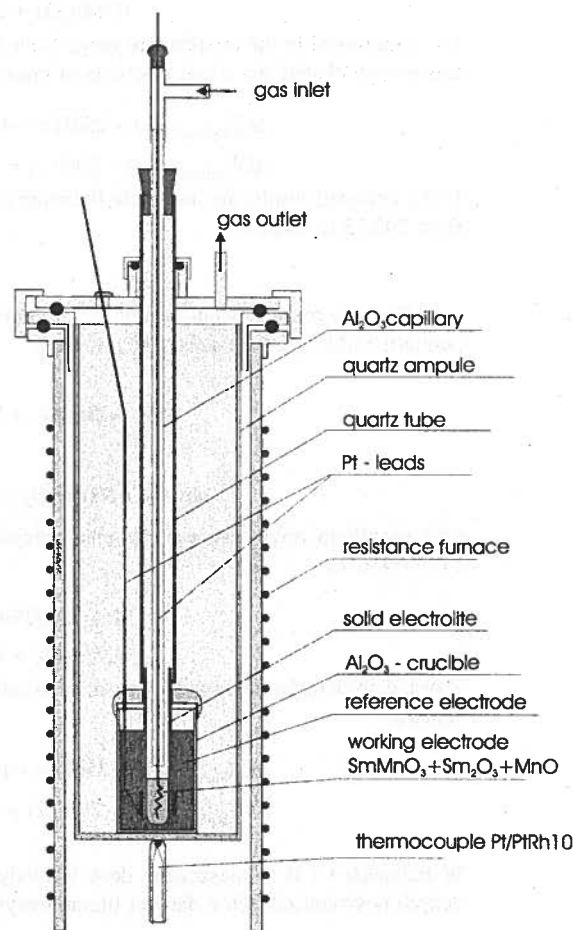$SmMnO_3$+Sm_2O_3+MnO

thermocouple Pt/PtRh10

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

In the cell I, 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 in argon atmosphere. The temperature of the furnace was controlled by Eurotherm temperature controller. E.m.f. was measured with high resistance multimeter Keithley 2000. The course of the experiment (e.m.f. vs. time necessary to reach the equilibrium) was recorded by a computer. The cell was working for about 2 weeks and the measurements were taken at increasing and decreasing temperatures.
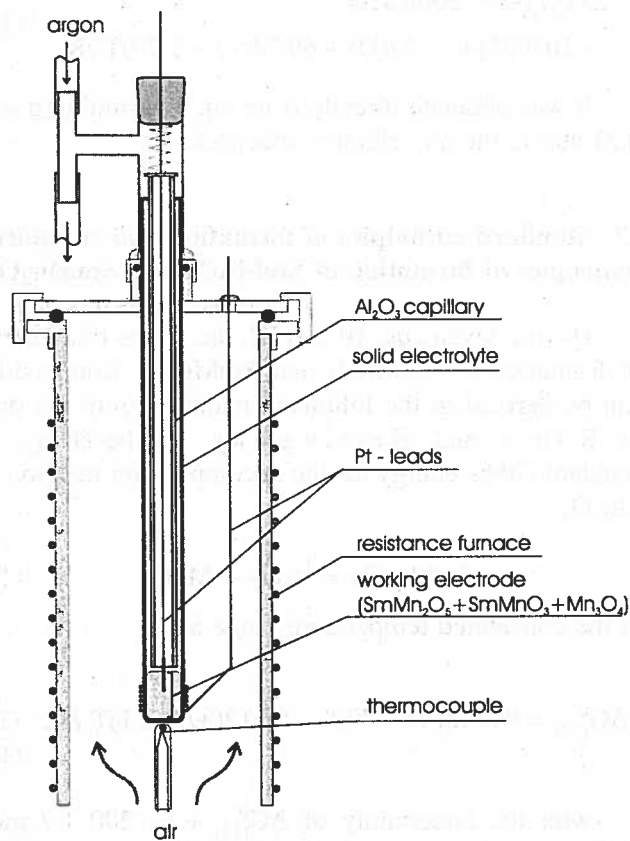

Fig. 2. Schematic diagram of the apparatus used for the emf measurements with cell II

In the cell II, the reference electrode was air that was flushing from outside a long tube of the solid electrolyte (Fig. 2). The working electrode consisted of a mixture of $SmMn_2O_5$, $SmMnO_3$ 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 e.m.f.'s were recorded in the same way as described before for the cell I. The whole experimental run took about two weeks.
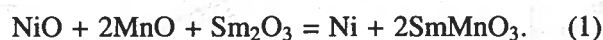
Principles.
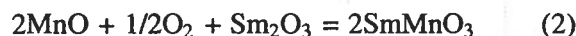
The following electrochemical cells were assembled:

$$MnO + Sm_2O_3 + SmMnO_3| \ O^{-2}|Ni + NiO \qquad \textbf{I}$$

and

$$Mn_3O_4 + SmMnO_3 + SmMn_2O_5|O^{-2}|air. \qquad \textbf{II}$$

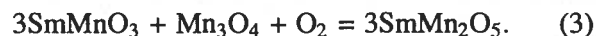The net cell reaction for the cell I is:

$$NiO + 2MnO + Sm_2O_3 = Ni + 2SmMnO_3. \qquad (1)$$

After the addition of the reaction of formation of NiO from pure elements, the reaction of formation of $SmMnO_3$:

$$2MnO + 1/2O_2 + Sm_2O_3 = 2SmMnO_3 \qquad (2)$$

is obtained.
For galvanic cell II the overall cell II reaction is:

$$3SmMnO_3 + Mn_3O_4 + O_2 = 3SmMn_2O_5. \qquad (3)$$

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 the Gibbs free energy from the following relationship:

$$\Delta G_{(1)} = -2FE_{(I)} = \Delta G_{(1)}^0 \qquad (4)$$

for the cell I, and

$$\Delta G_{(3)} = -4FE_{(II)} = \Delta G_{(3)}^0 - RT \cdot \ln (0.21) \qquad (5)$$

for the cell II, from which $\Delta G_{(3)}^0$ can be easily obtained:

$$\Delta G_{(3)}^0 = -4FE_{(II)} + RT \cdot \ln (0.21). \qquad (6)$$

The variations of the EMF's with temperature determined for the investigated systems are shown in Figures 3 and 4. The corresponding linear relations between EMF and temperature were obtained by the least-squares fit, and have the following form:

$$E_I(+/-0.7 \text{ mV}) = 150.2(+/-2.1) - 0.05778(+/-0.002)T \text{ /K} \qquad (7)$$

$$E_{II}(+/-5.3 \text{ mV}) =$$
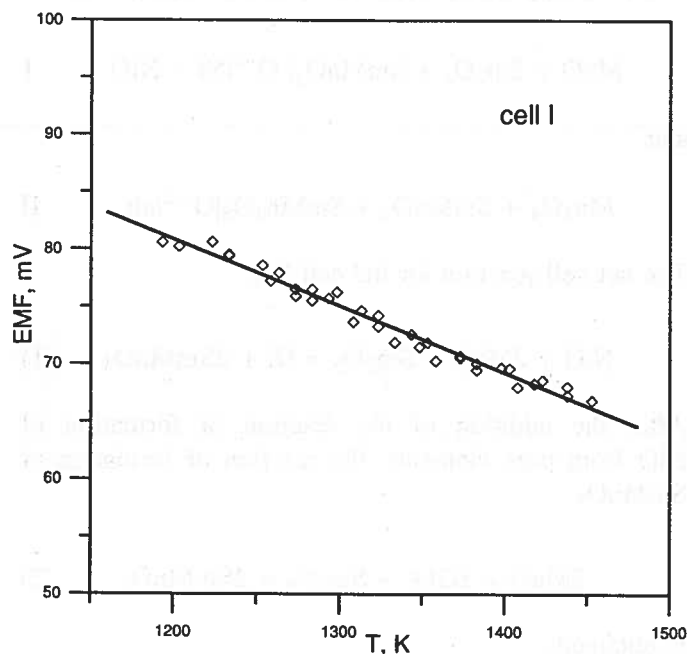$$832.2(+/-17) - 0.5756(+/-0.013)T \text{ /K}. \tag{8}$$

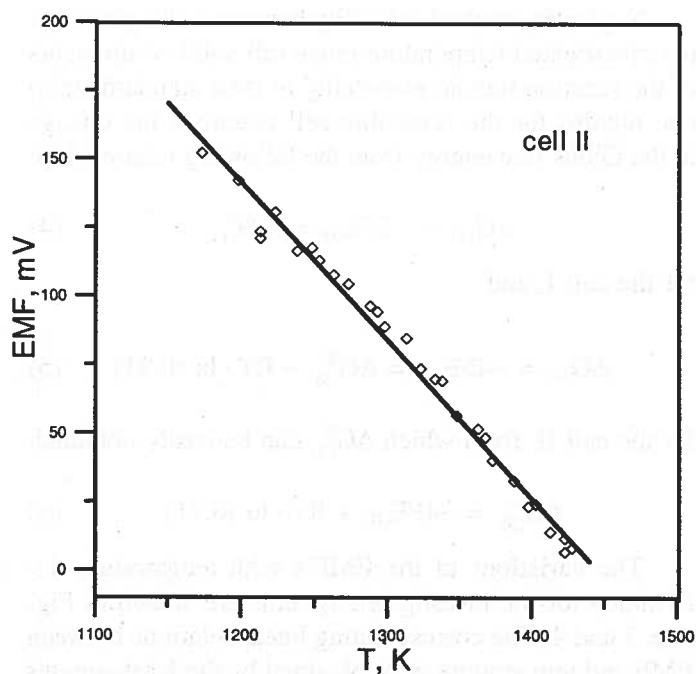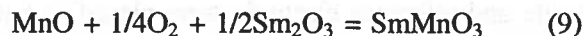Fig. 3. The emf vs. T plot obtained for cell I

Fig. 4. The emf vs. T plot obtained for cell II

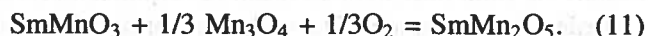Respective ΔG^0 change for reaction (2) after addition of $\Delta G_{f,NiO}^0$ (accepted after C h a r e t t e and F l e n g a s

[4] who also used e.m.f. measurements) yields Gibbs free energy change calculated per one mole of the phase formation:

$$MnO + 1/4O_2 + 1/2Sm_2O_3 = SmMnO_3 \tag{9}$$

in the form:

$$\Delta G_{(9)}^0 \ (+/-250\text{J}) =$$
$$-131321(+/-2000) + 48.02(+/-0.35)T\text{/K}. \tag{10}$$

Similarly, for the reaction:

$$SmMnO_3 + 1/3 \ Mn_3O_4 + 1/3O_2 = SmMn_2O_5. \tag{11}$$

Gibbs free energy change per one mole of the phase is:

$$\Delta G_{(11)}^0(+/-2000 \ \text{J}) =$$
$$-107085(+/-2200) + 69.74(+/-1.70)T\text{/K}. \tag{12}$$

It was obtained directly from eq. 6 assuming $p_{O2} = 0.21$ atm at the air reference electrode.

3. Standard enthalpies of formation and standard entropies of formation of SmMnO$_3$ and SmMn$_2$O$_5$

Having given eqs. 10 and 12, the Gibbs free energy of formation of SmMnO$_3$ and SmMn$_2$O$_5$ 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 [5] the change in standard Gibbs energy for the decomposition reaction of Mn$_2$O$_3$:

$$^1/_2Mn_2O_3 = {}^1/_4O_2 + MnO \tag{13}$$
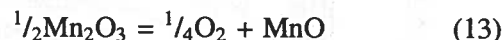
in the considered temperature range is:

$$\Delta G_{(13)}^0 = 91748(+/-700) - 51.12(+/-1.1)T\text{/K}. \tag{J} \tag{14}$$

with the uncertainty of $\Delta G_{(13)}^0 + /- 200$ J / mol. Adding reactions (9) and (13), the Gibbs energy of formation of SmMnO$_3$ from its component oxides:

$$^1/_2Sm_2O_3 + {}^1/_2Mn_2O_3 \Longrightarrow SmMnO_3 \tag{15}$$
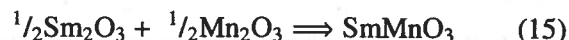
is given by:

$$\Delta G_{(15)}^0 = -39573(+/-2100) - 3.1(+/-1.15)T\text{/K} \quad \text{(J/mole)} \tag{16}$$

with the uncertainty estimated as +/− 350 J.

The temperature independent term in the last equation (16) represents the enthalpy of formation of $SmMnO_3$ phase from respective oxides at the mean experimental temperature 1300 K. Temperature dependent term is related to corresponding entropy change for the reaction of $SmMnO_3$ formation from oxides at the same temperature. Assuming that K o p p-N e u m a n n rule is valid, the resulting Δc_p for the solid state reaction is zero, and ΔH^0 is independent of temperature. Consequently, ΔH_{298}^0 is obtained as $- 39.57$ $(+/- 2.1)$ kJ/mol, and corresponding standard entropy change is 3.1 $(+/- 1.15)$ J/mol K at 298 K.

The enthalpy of formation of $SmMnO_3$ from its elements Sm, Mn and O_2 at 298 K can be obtained from evaluated above enthalpy change and the enthalpies of Sm_2O_3 and Mn_2O_3 given in compilation of P a n k r a t z [6] and R o b i e and H e m i n g w a y [5]. Its calculated value is equal to -1430.88 kJ/mol $(+/- 3.1)$. The standard entropy of $SmMnO_3$ at 298 K evaluated in the similar manner is 135.47 J/mol K $(+/- 2.4)$.
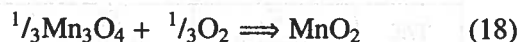
The Gibbs energy of formation of $SmMn_2O_5$ from binary oxides Sm_2O_3, Mn_2O_3 and MnO_2 due to reaction:

$$^1/_2Sm_2O_3 + {}^1/_2Mn_2O_3 + MnO_2 \Longrightarrow SmMn_2O_5 \quad (17)$$

can be evaluated in a similar way.

Having the Gibbs energy of formation of $SmMn_2O_5$ from $SmMnO_3$, Mn_3O_4 and O_2 according to reaction (11), and accepting standard Gibbs energy change re-

calculated in the previous study [3] for the reaction of Mn_3O_4 oxidation:

$$^1/_3Mn_3O_4 + {}^1/_3O_2 \Longrightarrow MnO_2 \quad (18)$$

for which:

$$\Delta G_{(18)}^0 = -57330(+/-1600)+68.43(+/-0.21)T/K \quad (19)$$

with the uncertainty of $\Delta G_{(18)}^0$ +/- 800 J, the addition of reactions (11), (15) and subtracting reaction (18) yields the Gibbs free energy of formation of $SmMn_2O_5$ from oxides Sm_2O_3, Mn_2O_3 and MnO_2 according to reaction (17):

$$\Delta G_{(17)}^0 = -89328(+/-3500)-1.79(+/-2.1)T/K \quad J/mol \quad (20)$$

with the uncertainty of +/-2200 J.

Applying again the K o p p-N e u m a n n rule to the reaction (17), the values of $\Delta H_{298}^0 = - 89.33$ $(+/-3.5)$ kJ/mol and $\Delta S_{298}^0 = 1.79$ $(+/-2.1)$ J/mol K are obtained. The enthalpy of formation of $SmMn_2O_5$ from its elements Sm, Mn, and O_2 at 298.15 K is $- 2000.63$ $(+/-3.8)$ kJ/mol. The standard entropy of $SmMn_2O_5$ at 298.15 K is 186.91 $(+/-3.0)$ J/mol K. Corresponding thermodynamic data for Sm_2O_3 were taken again after P a n k r a t z [6], while those for Mn_2O_3 and MnO_2 from R o b i e and H e m i n g w a y's paper [5].

TABLE 1

Thermodynamic data for $SmMnO_3$

T/K	C_p J/mol K	S_T^0 J/mol K	$H_T^0 - H_{298}^0$ kJ/mol	$S_T^0 - S_{298}$ J/mol K	fe f J/mol K	ΔH_f^0 kJ/mol	ΔG_f^0 kJ/mol
298.15	108.74	135.47	0	0	−135.47	−1430.88	−1349.81
400	117.36	168.77	11.562	33.306	−139.87	−1427.22	−1350.40
500	123.35	195.64	23.612	60.169	−148.41	−1423.45	−1333.02
600	128.13	218.56	36.193	83.095	−158.24	−1419.51	−1316.39
700	132.21	238.63	49.214	103.159	−168.32	−1415.43	−1300.41
800	135.85	256.52	62.620	121.054	−178.25	−1411.20	−1284.97
900	139.20	272.72	76.374	137.251	−187.86	−1406.86	−1270.02
1000	142.35	287.55	90.452	152.081	−197.09	−1404.62	−1255.43
1100	145.35	301.26	104.838	165.790	−205.95	−1400.07	−1241.03
1200	149.41	391.55	127.758	256.087	−285.09	−1391.28	−1126.70
1300	151.14	403.58	142.785	268.115	−293.75	−1386.25	−1104.85
1400	152.83	414.84	157.984	279.378	−302.00	−1391.26	−1082.28
1500	154.50	425.45	173.351	289.979	−309.88	−1384.61	−1058.65

TABLE 2
Thermodynamic data for $SmMn_2O_5$

T/K	C_p J/mol K	S_T° J/mol K	$H_T^\circ - H_{298}^\circ$ kJ/mol	$S_T^\circ - S_{298}$ J/mol K	fe f J/mol K	ΔH_f° kJ/mol	ΔG_f° kJ/mol
298.15	163.51	186.91	0	0	−186.91	−2000.63	−1864.29
400	180.58	237.60	17.607	50.69	−193.58	−1997.29	−1818.22
500	191.70	270.17	36.257	92.26	−206.66	−1993.65	−1773.87
600	199.34	314.84	55.830	127.93	−221.79	−1989.77	−1730.28
700	204.88	346.00	76.052	159.09	−237.36	−1985.78	−1687.35
800	209.19	373.66	96.761	186.74	−252.70	−1981.78	−1644.99
900	212.83	398.51	117.863	211.60	−267.55	−1977.82	−1603.13
1000	216.19	421.11	139.312	234.20	−281.80	−1976.15	−1561.67
1100	219.54	441.87	161.093	254.96	−295.42	−1972.31	−1520.41
1200	224.21	538.65	191.453	351.74	−379.10	−1964.35	−1472.28
1300	226.95	556.70	214.001	369.79	−392.08	−1960.02	−1431.46
1400	230.14	573.63	236.843	386.72	−404.46	−1961.71	−1385.77
1500	233.86	589.64	260.028	402.73	−416.28	−1945.94	−1333.11

Now, thermodynamic data tables for $SmMnO_3$ and $SmMn_2O_5$ can be derived from the information obtained in this study and from literature data. To do this, the data for MnO_2 had to be extrapolated up to 1400 K. 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 K o p p-N e u m a n n rule. The values of the Gibbs free energy function (f e f) are evaluated from component terms as $(G_T^0 - H_T^0)/T = -S_T^0 + (H_T^0 - H_{298.15}^0)/T$. The enthalpy of formation of $SmMnO_3$ and $SmMn_2O_5$ from the elements at each temperature is evaluated using the data assessed in this study for the two compounds and the values taken from Pankratz [6]. The Gibbs free energy of formation of $SmMnO_3$ and $SmMn_2O_5$ from elements is obtained at regular intervals of temperature using the relation $\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0$. Of course, these data can be further refined when both low-temperature and high-temperature experimental heat capacity values become available for these ternary oxides.

4. Discussion

In this work the thermodynamic stability of $SmMnO_3$ and $SmMn_2O_5$ phases was determined from e.m.f. measurements which were carried out in the temperature range from 1150 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 e.m.f.'s during temperature cycling as well as e.m.f's.

return to the previous value after the disturbance of the cell with small current passed through it. No side reaction was detected between zirconia tube and the oxides of the working electrode in the case of YSZ electrolyte. However, it should be mentioned that when CSZ electrolyte was used, samarium oxide was detected in the solid electrolyte by the microprobe.

Obtained Gibbs free energy changes for reactions of formation of $SmMnO_3$ and $SmMn_2O_5$ are shown and compared in Figures 5 and 6 with the results of the study of A t s u m i *et al* [7], S a t o h *et al* [8], K a m a - t a *et al.* [9] and K i t a y a m a *et al.* [10]. As far as the results obtained for $SmMnO_3$ phase are concerned, a good agreement is found between our study and previous results [7, 9, 10, 12], as shown in Fig. 5. It is seen that the results of Atsumi *et al.* are very close to the results of this study, differing slightly from our temperature dependence. Atsumi *et al.* [7] used also e.m.f. technique. They used Fe + FeO reference electrode and consequently their cells had to produce higher e.m.f.'s than those measured in this study. Such a choice of the reference electrode does not always mean higher precision of the measurements. Unfortunately, in their paper neither graphs nor equations of the e.m.f. vs. temperature plots are given. Therefore, it is difficult to assess the accuracy of their cell performance.

The discrepancy between results is much bigger in the case of $SmMn_2O_5$ phase (Fig. 6). It is obvious that temperature dependencies differ widely. Satoh *et al.* [8] applied thermogravimetry and differential thermal analysis under various oxygen partial pressure in order to determine decomposition temperature of respective $LnMn_2O_5$ phases. From the oxygen partial pressure

at the decomposition temperature Gibbs 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 from our values, especially at a lower temperature. In the study of K a m a t a *et al.* [9], K i t a y a m a *et al.* [10] and A t s u m i *et al* [12], Gibbs free energy changes for respective reactions are given only at single temperature. These values are also shown in the Figures 5 and 6 but they do not say anything about possible temperature dependence. However, it is seen that good agreement is also found between these values and the results of this study.
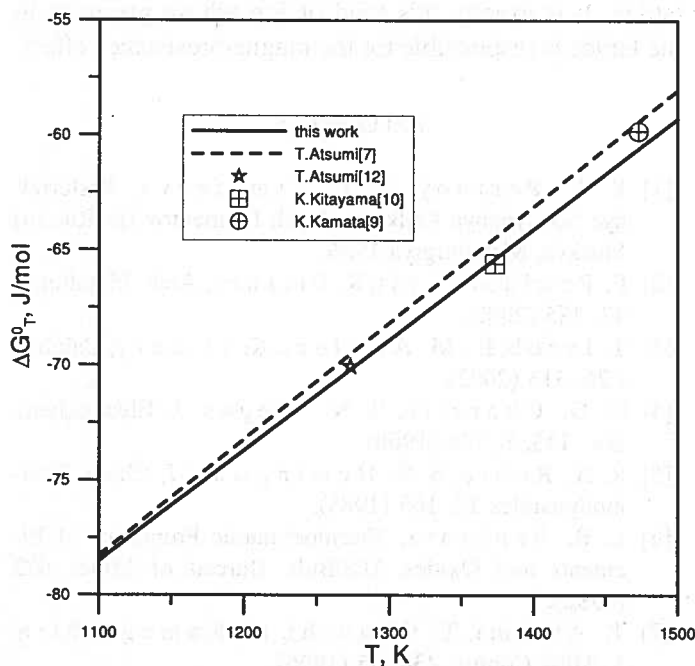
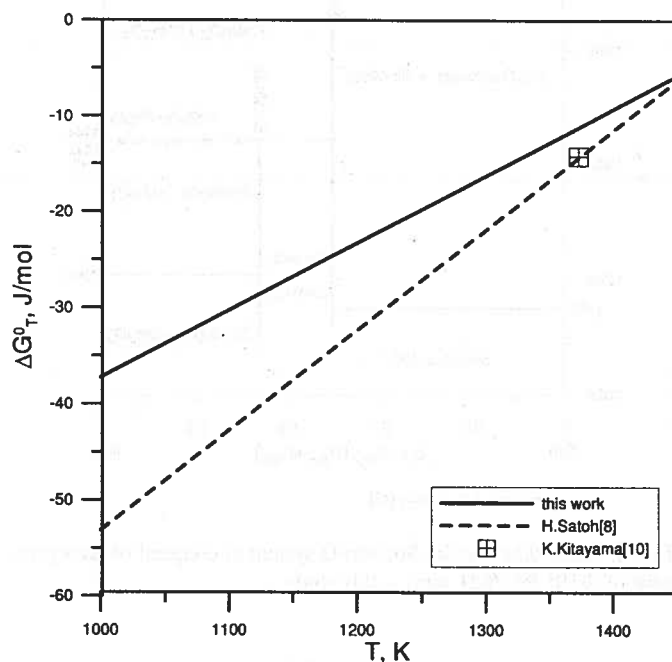ments, though there are some differences. The main reason is probably the nonstoichiometry of both phases.

Fig. 6. Comparison of Gibbs energy change of $SmMn_2O_5$ formation obtained in this study with the data reported in the literature

Fig. 5. Comparision of Gibbs energy change of $SmMnO_3$ formation obtained in this study with the data reported in the literature

Using the results of this study two different representations of phase equilibria in Sm-Mn-O system can be calculated and compared with experimental results of K i t a y a m a *et al* [10] and B a l a k i r e v *et al* [11]. One of them corresponds to phase relations at constant temperature 1373 K. The other one is calculated at constant pressure $p_{O2} = 0.21$ atm.. They are both shown in Fig. 7 and 8. The composition variable ζ is the molar fraction $n_{Mn}/(n_{Mn} + n_{Sm})$. It can be seen that calculated phase equilibria reflect the results of those experi-
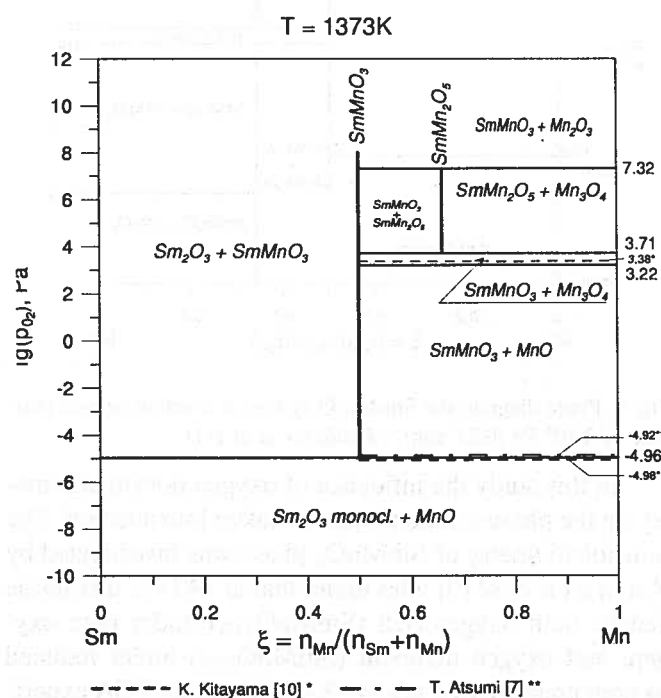

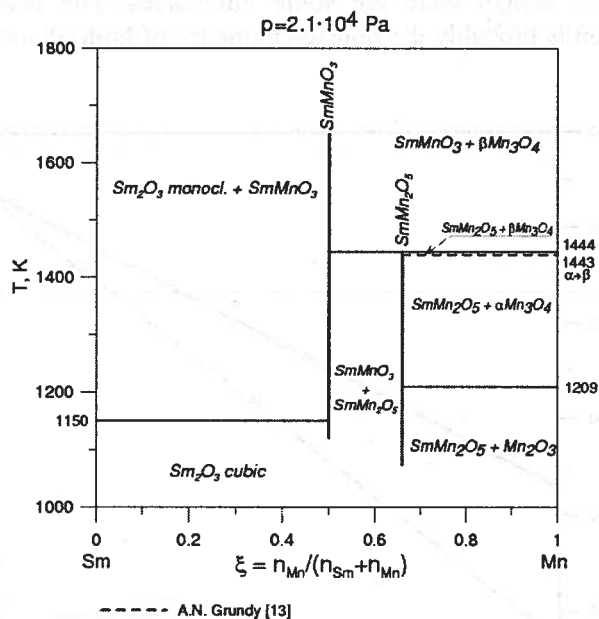Fig. 7. Phase diagram of the Sm-Mn-O system at constant temperature 1373K

Fig. 8. Phase diagram the Sm-Mn-O system at constant oxygen pressure of $2 \cdot 10^4$ Pa (0.21 atm) – this study
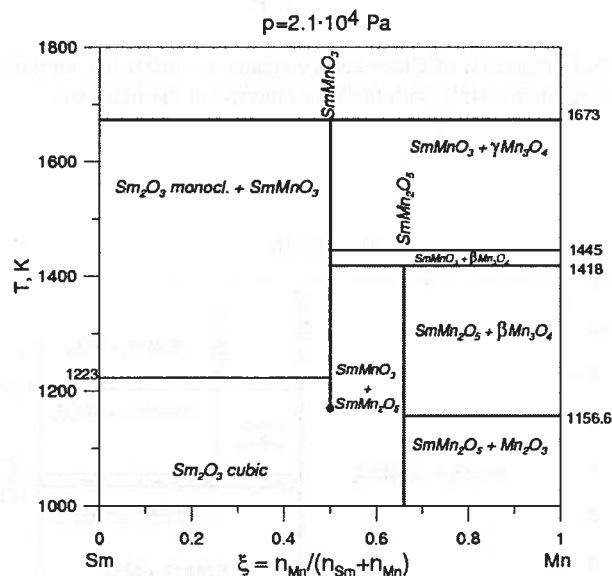

Fig. 9. Phase diagram the Sm-Mn-O system at constant oxygen pressure of $2 \cdot 10^4$ Pa (0.21 atm) – Balakirev at al [11]

In this study the influence of oxygen nonstoichiometry on the phase relations was not taken into account. The nonstoichiometry of $SmMnO_3$ phase was investigated by K a m a t a *et al* [9] who found that at 1473 K this phase can be both oxygen rich ($SmMnO_{3.03}$) under pure oxygen, and oxygen deficient ($SmMnO_{2.98}$) under reduced oxygen pressure ($\log p_{O2} = -8.47$). Running TGA experiments under gas mixtures Atsumi *et al* [12] demonstrated

that the lower limit of the phase stability at 1273 K and at $\log p_{O2} = -11.5$ is about 2.965. The $SmMn_2O_5$ phase can also be nonstoichiometric. K i t a y a m a *et al* [10] determined the composition $SmMn_2O_{4.92}$ at 1373 K and at $\log p_{O2} = -1.55$. They also suggested that the composition of $SmMnO_3$ solid solutions on the Sm_2O_3-rich side and that on the Sm_2O_3-poor side are not the same. It seems that $SmMnO_{3-\delta}$ solid solution can be found with an excess of Sm as well as of Mn. However, in our experiments $-\log p_{O2}$ varied between 13.4 and 8.9, which means that the solid solution kept approximately constant oxygen deficient composition.

There is no doubt that nonstoichiometric behaviour and phase stability are connected and the influence of nonstoichiometry on phase equilibria should also be experimentally established. It seems that a system ideal for electrochemical study of this kind of interdependence is Eu-Mn-O system. A t s u m i *et al* [12] demonstrated that $EuMnO_3$ phase has the largest oxygen excess at 1273 K., which results in the inclusion of Mn^{+4} ions into the lattice. It is exactly this kind of ion whose presence in the lattice is responsible for the magnetoresistance effect.

REFERENCES

[1] K. I. P o r t n o y, N. I. T i m o f e e v a, Kislorodnye Soedynenya Redkozemlnych Elementov (in Russin) Moskva, Metallurgiya 1986.

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

[3] T. J a c o b, K. M. A t t a l u r i, K. F i t z n e r, Calphad J. **26**, 313 (2002).

[4] G. G. C h a r e t t e, S. N. F l e g a s, J. Electrochem. Soc. **115**, 8, 796 (1968).

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

[6] L. B. P a n k r a t z, Thermodynamic Properties of Elements and Oxides, U.S.Bull. Bureau of Mines 672 (1982).

[7] 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. Alloy Comps. **238**, 35 (1996).

[8] H. S a t o h, S. S u z u k i, K. J a m a n o t o, N. K a m e g a s h i r a, J. Alloys Comps. **234**, 1 (1996).

[9] K. K a m a t a, T. N a k a j i m a, T. N a l u m u r a, Mat. Res. Bull. **14**, 1007 (1979).

[10] K. K i t a y a m a, M. K o b a y a s h i, T. K i m o t, J. Solid State Chem. **167**, 160 (2002).

[11] V. F. B a l a k i r e v, Yu. V. G o l i k o v, S. G. T i t o v a, Dokl. AN. RAN **377**(1), 67 (2001).

[12] T. A t s u m i, T. O h g u s h i, H. N i m i k o t a, N. K a m o g a s h i r a, J. Alloys Comps. **252**, 67 (1997).

[13] A. N. G r u n d y, B. H. H a l l s t e d t, L. J. G a u c k l e r, J. Phase Equilibria **24**(1), 21 (2003).