E. PAWLAS-FORYST*, K. T. JACOB**, K. FITZNER***

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:

\[ \text{MnO} + \text{Sm₂O₃} + \text{SmMnO₃} / \text{O}^{2-} / \text{Ni} + \text{NiO} \]

and

\[ \text{Mn₃O₄} + \text{SmMnO₃} + \text{SmMn₂O₅} / \text{O}^{2-} / \text{air} \]

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

\[ \text{MnO} + \frac{1}{2}\text{Sm₂O₃} + \frac{1}{4}\text{O₂} = \text{SmMnO₃} \]

\[ \frac{1}{3}\text{Mn₃O₄} + \text{SmMnO₃} + \frac{1}{3}\text{O₂} = \text{SmMn₂O₅} \]

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:

\[ \Delta G^0_{2\text{SmMnO₃}(+/- - 250)} = -131321(+/- - 2000) + 48.02(+/- - 0.35)T \text{ J / K} \]

\[ \Delta G^0_{2\text{SmMn₂O₅}(+/- - 2000)} = -107085(+/- - 2200) + 69.74(+/- - 1.70)T \text{ J / K} \]

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, wyznaczono metodą pomiaru SEM ogniw ze stałym elektrolitem:

\[ \text{MnO} + \text{Sm₂O₃} + \text{SmMnO₃} / \text{O}^{2-} / \text{Ni} + \text{NiO} \] ogniwo I

\[ \text{Mn₃O₄} + \text{SmMnO₃} + \text{SmMn₂O₅} / \text{O}^{2-} / \text{powietrze} \] ogniwo II

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

\[ \text{MnO} + \frac{1}{2}\text{Sm₂O₃} + \frac{1}{4}\text{O₂} = \text{SmMnO₃} \]

\[ \frac{1}{3}\text{Mn₃O₄} + \text{SmMnO₃} + \frac{1}{3}\text{O₂} = \text{SmMn₂O₅} \]

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

\[ \Delta G^0_{3\text{SmMnO₃}(+/- - 250)} = -131321(+/- - 2000) + 48.02(+/- - 0.35)T \text{ J / K} \]

\[ \Delta G^0_{3\text{SmMn₂O₅}(+/- - 2000)} = -107085(+/- - 2200) + 69.74(+/- - 1.70)T \text{ J / K} \]

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

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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$_2$O$_5$ and Ln$_2$MnO$_4$ 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$_2$O$_5$ 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$_2$O$_3$ (99.999% from Johnson Matthey Co.), MnO (99.9%), Mn$_2$O$_3$ (99% from Aldrich) and Mn$_3$O$_4$ (prepared by heating of Mn$_2$O$_3$ under proper conditions) were used as starting materials to prepare respective phases. Sm$_2$O$_3$ was dried in air at 1123K for 26 hours. Mn$_2$O$_3$ was calcined in air at 1023K for 70 hours. Next, an equimolar mixture of Sm$_2$O$_3$ and Mn$_2$O$_3$ 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$_2$O$_3$ 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$_3$O$_5$ using previously prepared SmMnO$_3$, Mn$_2$O$_3$ and Mn$_3$O$_4$ as substrates. The equimolar mixtures of SmMnO$_3$-Mn$_2$O$_3$ and SmMn$_3$O$_4$-Mn$_3$O$_4$ 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$_2$O$_5$ was the main product of the reaction; in the samples we found also small amounts of Mn$_2$O$_4$ and SmMnO$_3$. We used this product of the synthesis, after the addition of SmMnO$_3$ and Mn$_3$O$_4$, 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$_2$O$_3$ + MnO phases as the working electrode, and the second one was used to determine the e.m.f. produced by the cell with SmMn$_2$O$_5$ + SmMnO$_3$ + Mn$_3$O$_4$ working electrode (Fig. 2).

![Fig. 1. Schematic diagram of the apparatus used for the emf measurements with cell I](image-url)
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.

Principles.

The following electrochemical cells were assembled:

\[
\text{MnO + Sm}_2\text{O}_3 + \text{SmMnO}_3 \mid \text{O}^{-2}\text{[Ni + NiO I}
\]

and

\[
\text{Mn}_3\text{O}_4 + \text{SmMnO}_3 + \text{SmMn}_2\text{O}_5 \mid \text{O}^{-2}\text{[air. II}
\]

The net cell reaction for the cell I is:

\[
\text{NiO + 2MnO + Sm}_2\text{O}_3 = \text{Ni + 2SmMnO}_3. \quad (1)
\]

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

\[
2\text{MnO} + 1/2\text{O}_2 + \text{Sm}_2\text{O}_3 = 2\text{SmMnO}_3 \quad (2)
\]

is obtained.

For galvanic cell II the overall cell II reaction is:

\[
3\text{SmMnO}_3 + \text{Mn}_3\text{O}_4 + \text{O}_2 = 3\text{SmMn}_2\text{O}_5. \quad (3)
\]

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:

\[
\Delta G_{(1)} = -2FE_{(0)} = \Delta G_{(1)}^0 \quad (4)
\]

for the cell I, and

\[
\Delta G_{(3)} = -4FE_{(0)} = \Delta G_{(3)}^0 = RT \cdot \ln (0.21) \quad (5)
\]

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

\[
\Delta G_{(3)}^0 = -4FE_{(0)} + RT \cdot \ln (0.21). \quad (6)
\]

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:

\[
E_f (+/- 0.7 \text{mV}) = 150.2(+/- 2.1) - 0.05778(+/- 0.002)T /\text{K} \quad (7)
\]
\[ E_n(+/ - 5.3 \text{ mV}) = 832.2(+/ - 17) - 0.5756(+/ - 0.013)T /\text{K}. \] (8)

\[ \text{MnO} + 1/4\text{O}_2 + 1/2\text{Sm}_2\text{O}_3 = \text{SmMnO}_3 \] (9)

in the form:

\[ \Delta G^0_{(9)}(+/ - 250 J) = -131321(+/ - 2000) + 48.02(+/ - 0.35)T/\text{K}. \] (10)

Similarly, for the reaction:

\[ \text{SmMnO}_3 + 1/3 \text{Mn}_3\text{O}_4 + 1/3\text{O}_2 = \text{SmMn}_2\text{O}_5. \] (11)

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

\[ \Delta G^0_{(11)}(+/ - 2000 J) = -107085(+/ - 2200) + 69.74(+/ - 1.70)T/\text{K}. \] (12)

It was obtained directly from eq. 6 assuming \( p_{\text{O}_2} = 0.21 \text{ atm} \) at the air reference electrode.

3. Standard enthalpies of formation and standard entropies of formation of \( \text{SmMnO}_3 \) and \( \text{SmMn}_2\text{O}_5 \)

Having given eqs. 10 and 12, the Gibbs free energy of formation of \( \text{SmMnO}_3 \) and \( \text{SmMn}_2\text{O}_5 \) from oxides can be derived in the following manner. From the data of Robie and Hemingway [5] the change in standard Gibbs energy for the decomposition reaction of \( \text{Mn}_2\text{O}_3 \):

\[ \frac{1}{2}\text{Mn}_2\text{O}_3 = \frac{1}{4}\text{O}_2 + \text{MnO} \] (13)

in the considered temperature range is:

\[ \Delta G^0_{(13)} = 91748(+/ - 700) - 51.12(+/ - 1.1)T /\text{K}. \] (14)

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

\[ \frac{1}{2}\text{Sm}_2\text{O}_3 + \frac{1}{2}\text{Mn}_2\text{O}_3 \rightarrow \text{SmMnO}_3 \] (15)

is given by:

\[ \Delta G^0_{(15)} = -39573(+/ - 2100) - 3.1(+/ - 1.15)T/\text{K} \] (J/mole) (16)

with the uncertainty estimated as \( +/- 350 \text{ J} \).
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 Koppen rule is valid, the resulting $\Delta c_p$ for the solid state reaction is zero, and $\Delta H^0$ is independent of temperature. Consequently, $\Delta H^0_{298}$ 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$_2$O$_3$ and Mn$_2$O$_3$ given in compilation of Pankratz [6] and Robie and Hemingway [5]. Its calculated value is equal to $-1430.88$kJ/mol (+/- 3.1 kJ/mol). 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$_2$O$_5$ from binary oxides Sm$_2$O$_3$, Mn$_2$O$_3$ and MnO$_2$ due to reaction:

$$\frac{1}{2} \text{Sm}_2\text{O}_3 + \frac{1}{2} \text{Mn}_2\text{O}_3 + \text{MnO}_2 \rightarrow \text{SmMn}_2\text{O}_5$$

(17)

can be evaluated in a similar way.

Having the Gibbs energy of formation of SmMn$_2$O$_5$ from SmMnO$_3$, Mn$_3$O$_4$ 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$_3$O$_4$ oxidation:

$$\frac{1}{3} \text{Mn}_3\text{O}_4 + \frac{1}{3} \text{O}_2 \rightarrow \text{MnO}_2$$

(18)

for which:

$$\Delta G^0_{18} = -57330(+/-1600) + 68.43(+/-0.21) \text{T/K}$$

(19)

with the uncertainty of $\Delta G^0_{18}$ (+/- 800 J, the addition of reactions (11), (15) and subtracting reaction (18) yields the Gibbs free energy of formation of SmMn$_2$O$_5$ from oxides Sm$_2$O$_3$, Mn$_2$O$_3$ and MnO$_2$ according to reaction (17):

$$\Delta G^0_{17} = -89328(+/-3500) - 1.79(+/-2.1) \text{T/K J/mol}$$

(20)

with the uncertainty of +/- 2200 J.

Applying again the Koppen rule to the reaction (17), the values of $\Delta H^0_{298} = -89.33$ (+/- 3.5) kJ/mol and $\Delta S^0_{298} = 1.79$ (+/- 2.1) J/mol K are obtained. The enthalpy of formation of SmMn$_2$O$_5$ from its elements Sm, Mn, and O$_2$ at 298.15 K is $-2000.63$ (+/- 3.8) kJ/mol. The standard entropy of SmMn$_2$O$_5$ at 298.15 K is 186.91 (+/- 3.0) J/mol K. Corresponding thermodynamic data for Sm$_2$O$_3$ were taken again after Pankratz [6], while those for Mn$_2$O$_3$ and MnO$_2$ from Robie and Hemingway’s paper [5].

**TABLE 1**

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Now, thermodynamic data tables for SmMnO\(_3\) and SmMn\(_2\)O\(_5\) 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 a polynomial relationship. The values of the Gibbs free energy function \((f \epsilon f)\) 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 SmMnO\(_3\) and SmMn\(_2\)O\(_5\) 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\(_2\)O\(_5\) from elements is obtained at regular intervals of temperature using the relation \( \Delta G^0 = \Delta H^0 - T \Delta S^0 \). 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\(_2\)O\(_5\) 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 microprobe.

Obtained Gibbs free energy changes for reactions of formation of SmMnO\(_3\) and SmMn\(_2\)O\(_5\) are shown and compared in Figures 5 and 6 with the results of the study of Atsumi et al. [7], Satoh et al. [3], Kamae et al. [9] and Itaya 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\(_2\)O\(_5\) 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\(_2\)O\(_5\) \) 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 Kamata et al. [9], Kitayama et al. [10] and Atsumi 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.

Fig. 5. Comparison of Gibbs energy change of SmMnO₃ 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 Kitayama et al [10] and Balakirev et al [11]. One of them corresponds to phase relations at constant temperature 1373 K. The other one is calculated at constant pressure pO₂ = 0.21 atm.. They are both shown in Fig. 7 and 8. The composition variable \( \xi \) is the molar fraction \( n_{Mn}/(n_{Sm} + n_{Mn}) \). It can be seen that calculated phase equilibria reflect the results of those experiments, though there are some differences. The main reason is probably the nonstoichiometry of both phases.

Fig. 6. Comparison of Gibbs energy change of SmMn₂O₅ formation obtained in this study with the data reported in the literature

Fig. 7. Phase diagram of the Sm-Mn-O system at constant temperature 1373K
that the lower limit of the phase stability at 1273 K and at log $p_{O_2} = -11.5$ is about 2.965. The SmMn$_2$O$_5$ phase can also be nonstoichiometric. Kitayama et al [10] determined the composition SmMn$_2$O$_{4.92}$ at 1373 K and at log $p_{O_2} = -1.55$. They also suggested that the composition of SmMn$_2$O$_5$ solid solutions on the Sm$_2$O$_3$-rich side and that on the Sm$_2$O$_3$-poor side are not the same. It seems that SmMn$_{0.5}$O$_{3.5}$ solid solution can be found with an excess of Sm as well as of Mn. However, in our experiments -log $p_{O_2}$ 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. Atsumi 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


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