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High-temperature enthalpy and heat capacity of $ErMnO_3$

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Abstract

The heat capacity of $ErMnO_3$ was measured by differential scanning calorimetry (DSC) from 300 K to about 850 K. The heat capacity value at 298 K was determined to be $103.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$. In order to obtain thermodynamic data at higher temperatures, the enthalpy change of $ErMnO_3$, $H^0_T-H^0_{298}$, was measured in the temperature range 673–1373 K by the drop method. The accuracy of the enthalpy measurement was checked by comparing the measured enthalpy changes of Er_2O_3 and Mn_2O_3 with literature values. The relative error was ± 2% for both compounds. However, for the heat capacity calculated from the enthalpy change, the maximum deviation of the heat capacity from the references was ± 3%. The equation for the heat capacity of $ErMnO_3$ derived by combining the two methods (DSC and drop methods) was $C_p = 111.9 + 26.4 \times 10^{-3}T - 1.33 \times 10^6 T^{-2}$ from 298 to 1373 K. The standard Gibbs free energy of formation for $ErMnO_3$, $-1362.7\,\mathrm{kJ\,mol^{-1}}$ at 298 K, was also calculated using the above data.

Keywords: DSC; Enthalpy; $ErMnO_3$; Heat Capacity

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1. Introduction

Recently, ABO_3-type compounds have been studied extensively as possible electrode materials in solid oxide fuel cells [1]. However, few reports of high-temperature thermodynamic data for those compounds were seen. About $LnMnO_3$ (Ln = rare earth) Kamata et al. [2, 3] reported the thermogravimetric analysis of $LnMnO_3$ (Ln = La, Sm, Dy, Y, Er, Yb) and described that non-stoichiometry of $LaMnO_3$ was very wide, while that of compound except $LaMnO_3$ was a moderately narrow. Gibbs free energy change for the following reaction was evaluated from the oxygen partial

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pressure of decomposition at 1473 K [2, 3]

$$LnMnO_3 \rightarrow 1/2\,Ln_2O_3 + MnO + 1/4\,O_2 \tag{1}$$

The Gibbs free energy changes for the above reactions were also studied for several rare earths using thermogravimetric analysis [4, 5], solid state cell [6] or the electrical conductivity method [6–11]. Yokokawa et al. [12] estimated several thermodynamic properties of $LnMnO_3$ compounds and registered those properties to Thermodynamic Data Base MALT2 [13]. But most of these properties for rare earth manganites have not been measured. For an exact discussion on the thermodynamic stabilities of these materials at high temperature it is necessary to carry out the thermal measurements and to obtain the experimental data. As one of a series of work to collect the thermodynamic properties on the rare earth manganites, heat capacity and enthalpy of $ErMnO_3$ which has a small nonstoichiometry [3] in comparison with $LaMnO_3$ were measured by DSC and drop methods, respectively. The temperature dependence of the heat capacity for $ErMnO_3$ was derived and several thermodynamic properties were evaluated.

2. Experimental

The Er_2O_3 and Mn_2O_3 used in these measurements had a purity of 99.99% (Rare Metallic Co. Ltd.). Er_2O_3 was heated in Ar at 1273 K for 24 h in order to dry. Mn_2O_3 was prepared by heating at 1073 K in air for three days in order to dry and to adjust stoichiometry and then quenched to room temperature. $ErMnO_3$ was synthesized by heating mixtures of Er_2O_3 and Mn_2O_3 at 1573 K in air for three days. The prepared specimens were identified by powder X-ray diffractometry [14–16].

The DSC apparatus used for the heat capacity measurements was a DSC-200 model of Seiko Electronic Industry Co., Ltd. connected with a personal computer. A sampling interval was every 1 K. The detailed procedure of heat capacity measurement with DSC was mentioned in the previous papers [17, 18]. Accuracy of the measurement was within $\pm 2.5\%$.

An apparatus of drop method was made out by quoting the literature [19]. The apparatus is schematically shown in Fig. 1. The apparatus consists of three parts; water calorimeter, sample heating and drop mechanism parts. Water calorimeter part is made by a copper cylinder, closed at the bottom, of 25 mm inner diameter, 270 mm length and 2 mm thickness, attached to twenty copper fins for rapid thermal exchange. The size of fin is 100 mm of diameter and 0.55 mm of thickness. 2 kg of distilled water is put into the cylinder inside a Dewar bottle surrounded by thermal insulating material. In order to achieve thermal exchange smoothly, a stirrer with a constant rotation rate is attached to the Dewar bottle. The temperature rise due to the rotation of its screw was less than 5×10^{-3} K per minute. Temperature of water was read out by a quartz thermometer. A shutter is attached to the upper part of the calorimeter to prevent thermal radiation from the furnace. The sample heating part is a furnace made of a kanthal wire and alumina tube. The temperature of the sample in the furnace is

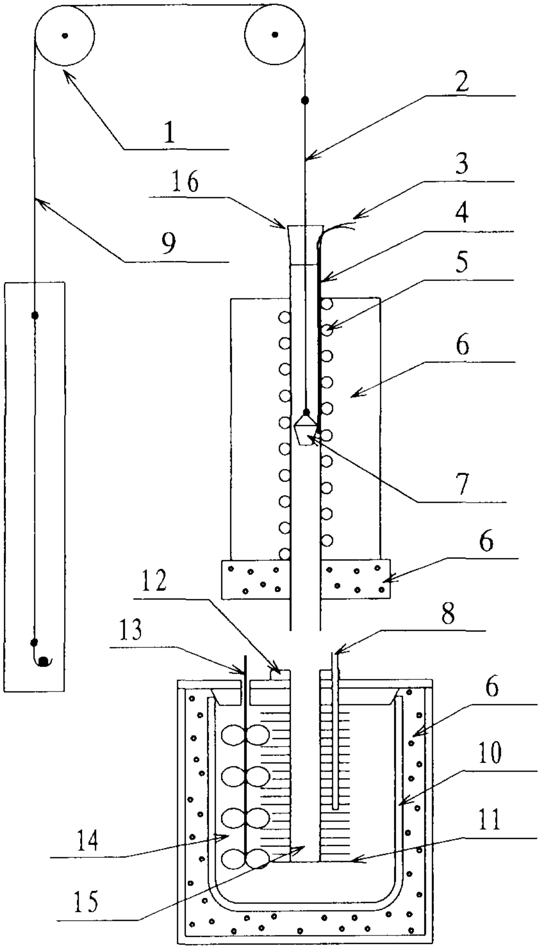

Fig. 1. Illustration of the apparatus: 1, pulley; 2, Pt-13%Rh wire; 3, Pt/Pt-13%Rh thermocouple; 4, Al_2O_3 tube; 5, heater; 6, insulating material; 7, Pt crucible; 8, quartz thermometer; 9, cotton thread; 10, Dewar bottle; 11, copper fins; 12, shutter; 13, stirrer; 14, pure water; 15, copper cylinder; and 16, cap.

measured with a platinum/platinum-13% rhodium thermocouple. Temperature control is within ± 1 deg, while a homogeneous region of temperature within ± 1 deg is about 2 cm (the same length as platinum crucible) near center of the furnace. Hence, the fluctuation of the temperature of the specimen is kept within ± 2 deg. The sample is put in a platinum crucible and suspended by a platinum-13% rhodium wire in location of the homogeneous region. The drop mechanism part consists of the pulleys and the platinum-13% rhodium wire. A procedure for the measurement and a treatment of the data are as follows. Before the measurement of the sample, the measurements for α-Al_2O_3 were carried out to calibrate the apparatus. The sample is equilibrated for a time more than thirty minutes at a given temperature. After the shutter is opened, the sample is rapidly dropped into the calorimeter part from the sample heating part and the shutter is immediately closed. Heat released from both of the sample and the platinum crucible is transferred to water through fins and the temperature rise of water is read out at every thirty seconds from 5 minutes prior to dropping operation until the temperature change approaches the initial state. Initial temperature of water in the calorimeter is adjusted in order that the final temperature becomes 298 K. The observed amount of heat was calculated by the following Eq. (1):

$$Q(\alpha\text{-Al}_2\text{O}_3 + \text{Pt}) = w \cdot C_p \cdot \Delta T \tag{2}$$

where, $Q(\alpha\text{-Al}_2\text{O}_3 + \text{Pt})$ is the observed heat of the experimental system including $\alpha\text{-Al}_2\text{O}_3$ specimen and platinum crucible, w is the amount of water in the calorimeter, and C_p is heat capacity of water [13] and ΔT is a quantity of temperature rise. At one experimental temperature, $Q(\alpha\text{-Al}_2\text{O}_3 + \text{Pt})$ is connected with the actual released heat as follows.

$$\begin{aligned} Q(\alpha\text{-Al}_2\text{O}_3 + \text{Pt}) = k[&n(\alpha\text{-Al}_2\text{O}_3)(H_T^0 - H_{298}^0) \\ &\times (\alpha\text{-Al}_2\text{O}_3) + n(\text{Pt})(H_T^0 - H_{298}^0)(\text{Pt})] \end{aligned} \tag{3}$$

where, k is the calibration constant at that temperature, $n(\alpha\text{-Al}_2\text{O}_3)$ and $n(\text{Pt})$ are the number of moles of $\alpha\text{-Al}_2\text{O}_3$ and Pt, respectively, and $(H_T^0 - H_{298}^0)(\alpha\text{-Al}_2\text{O}_3)$ and $(H_T^0 - H_{298}^0)(\text{Pt})$ are heat contents of $\alpha\text{-Al}_2\text{O}_3$ and Pt at the experimental temperature obtained from MALT2 [13], respectively. The experiments were performed at least 3 times at each temperature. The similar experiment for the sample was carried out. Using the calibrated k value calculated from Eq. (3) at a given temperature, the enthalpy of the sample can be obtained from the Eq. (4)

$$\{H_T^0 - H_{298}^0\}(\text{sample}) = \frac{\dfrac{Q(\text{sample} + \text{Pt})}{k} - n(\text{Pt}) \times \{H_T^0 - H_{298}^0\}(\text{Pt})}{n(\text{sample})} \tag{4}$$

where $Q(\text{sample} + \text{Pt})$ is the observed amount of heat for the experimental system including the sample and the platinum crucible, $\{H_T^0 - H_{298}^0\}(\text{sample})$ is heat content of the sample at a given temperature and $n(\text{sample})$ is the number of moles of the sample. In the experiment for the determination of the calibration constant k, the amount of $\alpha\text{-Al}_2\text{O}_3$ was adjusted to obtain the same amounts of heat as the sample. The weights of the samples to be measured were 17.038 g for Er_2O_3, 7.024 g for Mn_2O_3 and 12.825 g for ErMnO_3. All of the samples were a little change of weight before and after the experiment, which was less than 0.01%. The temperature dependence of the enthalpy, which was determined from the experimental data at every 50 K of intervals from 673 to 31373 K, was derived by the same method as Venugopal et al. [20]. In this case, $(H_T^0 - H_{298}^0)/(T - 298)$ was plotted against experimental temperature and C_p at 298 K from the reference values or the present DSC method were also adopted on the graph, because the value of $(H_T^0 - H_{298}^0)/(T - 298)$ is C_{p298} at

$T = 298$ K. Thus the temperature dependences of enthalpy and heat capacity are expressed as follows.

$$H_T^0 - H_{298}^0 = a \cdot T + b \cdot T^2 + \frac{c}{T} + d \tag{5}$$

$$C_p = a + 2bT - \frac{c}{T^2} \tag{6}$$

Other thermodynamic properties can be calculated, if the Gibbs free energy change, such as reported by Kamata et al. is available. The Gibbs free energy change is expressed

$$\Delta G_T^0 = \Delta H_T^0 - T \cdot \Delta S_T^0 \tag{7}$$

where ΔH_T^0 and ΔS_T^0 were enthalpy and entropy changes of the Eq. (1) at temperature T, respectively. Provided ΔH_T^0 and ΔS_T^0 are expressed as functions of C_p, the result becomes

$$\Delta G_T^0 = \Delta G_{298}^0 + \int_{298}^{T} \Delta C_p dT - T \cdot \int_{298}^{T} \frac{\Delta C_p}{T} dT - (T - 298) \cdot \Delta S_{298}^0 \tag{8}$$

where ΔC_p is $\Delta C_p = 1/2\ C_p(Er_2O_3) + C_p(MnO) + 1/4 C_p(O_2) - C_p(ErMnO_3)$, according to Eq. (1). From this relation, the Gibbs free energy change of the decomposition reaction of the Eq. (1) at 298 K, ΔG_{298}^0 of Eq. (8), is derived if ΔS_{298}^0 is known. Then if the Gibbs free energy of formation at 298 K for Er_2O_3 and MnO are known, the Gibbs free energy of formation at 298 K for $ErMnO_3$ can be calculated from the relation,

$$\Delta G_{f,298}^0(ErMnO_3) = \tfrac{1}{2}\Delta G_{f,298}^0(Er_2O_3) + \Delta G_{f,298}^0(MnO) - \Delta G_{298}^0 \tag{9}$$

3. Results and discussion

As described above, the enthalpies of Er_2O_3 and Mn_2O_3 by the drop method were measured in order to check the accuracy of the present measurement. The measurement of Mn_2O_3 was carried out below 1123 K, because Mn_2O_3 decomposes to Mn_3O_4 above 1123 K under air atmosphere. The observed values of enthalpy for Er_2O_3 and Mn_2O_3 are listed in Table 1. The experimental results for Er_2O_3 are shown in Fig. 2(a) in comparison with the results by Pankratz and King [21] and Tsagareishvili and Gvelesiani [22], and those for Mn_2O_3 are shown in Fig. 3(a) with the data by Orr [23]. From these figures, it can be seen that the observed values of Er_2O_3 and Mn_2O_3 are in good agreement with the values of each reference. The relative deviations against each reference are shown in Fig. 2(b) for Er_2O_3 and Fig. 3(b) for Mn_2O_3, respectively. In Fig. 2, our results for Er_2O_3 are between those of Pankratz and King [21] and Tsagareishvili and Gvelesiani [22]. It was found that the accuracy for the enthalpy measurement with the present drop apparatus was ± 2.0%. The heat capacity of Er_2O_3 at 298 K, C_{p298}, is 108.5 J mol^{-1} K^{-1} by the adiabatic calorimetry by Westrum Jr. and Justice [24]. Using this value, the temperature dependence of the heat capacity of

Table 1
The observed enthalpies of Er_2O_3 and Mn_2O_3

Er_2O_3		Mn_2O_3	
T/K	$H_T^0 - H_{298}^0$/kJ mol^{-1}	T/K	$H_T^0 - H_{298}^0$/kJ mol^{-1}
672.7	45.15	673.5	42.25
723.2	51.74	723.6	49.35
773.1	57.85	772.6	55.27
823.4	64.30	821.9	62.73
873.4	70.46	872.9	68.72
923.2	76.35	923.4	74.83
971.9	82.85	973.1	82.20
1023.4	90.22	1022.9	89.09
1073.7	96.21	1073.1	95.94
1123.3	103.6	1123.4	103.6
1173.2	111.2		
1223.1	116.1		
1273.5	123.2		
1323.6	130.4		
1374.8	138.6		

Er_2O_3 above room temperature was calculated from the enthalpy data with Eq. (6) by the same procedure as Venugopal et al. [20].

$$C_p(Er_2O_3) = 121.9 + 11.0 \times 10^{-3}T - 1.47 \times 10^6 T^{-2} \quad (298 \sim 1375\,K) \qquad (10)$$

Since Mn_2O_3 has a phase transition at 307 K, the measured enthalpy changes of Mn_2O_3, $H_T^0 - H_{298}^0$, was converted to $H_T^0 - H_{325}^0$ according to the similar treatment as Robie and Hemingway [25]. In this case the heat capacity of Mn_2O_3 was measured by DSC method above room temperature and the C_{p325} of Mn_2O_3 was determined to be 101.7 J mol^{-1} K^{-1}. According to Robie and Hemingway, C_{p325} is 103.5 J mol^{-1} K^{-1} by the adiabatic calorimetry and the result of this work is in good agreement with their result. Then, that of Mn_2O_3 was calculated in a similar procedure. The result for Mn_2O_3 was

$$C_p(Mn_2O_3) = 99.1 + 41.6 \times 10^{-3}T - 1.16 \times 10^6 T^{-2} \quad (298 \sim 1123\,K) \qquad (11)$$

These results are plotted in Fig. 4 for Er_2O_3 and in Fig. 5 for Mn_2O_3 together with each corresponding references [21–25] and results of DSC measurement. In Fig. 4, deviation from the values of references [21, 22] was ± 3%, while in Fig. 5, that from reference [25] was ± 2%, and that from DSC ± 3%. Hence, it is considered that the accuracy of the heat capacity value calculated from the enthalpy was within ± 3%. Therefore the present results are in a fair agreement with the results from other measurements.

The enthalpy of $ErMnO_3$ was measured and the results are listed in Table 2. The heat capacity was determined from C_{p298} in the same way. The value of C_{p298} of $ErMnO_3$

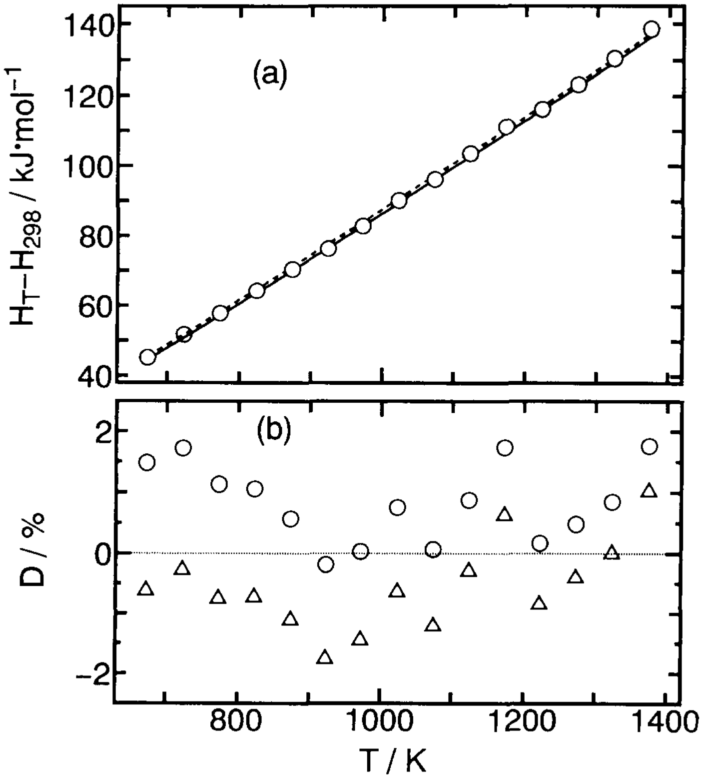

Fig. 2. (a) Enthalpies of Er_2O_3: solid and broken lines indicate the results by Tsagareishvili and Gvelesiani [22] and Pankratz and King [21], respectively; ○, this study. (b) Relative deviation of the values of this study from the literature values: ○, Tsagareishvili and Gvelesiani [22]; △, Pankratz and King [21].

was estimated from the result of multiple regression analysis for the heat capacity obtained from DSC measurement above room temperature. The equation for the heat capacity obtained from DSC was

$$C_p = 117.2 + 19.8 \times 10^{-3}T - 1.72 \times 10^6 T^{-2} \quad (310 \sim 863\,\mathrm{K}) \tag{12}$$

and the estimated value of C_{p298} from this equation was 103.7 J mol^{-1} K^{-1}. Combining this value with the present enthalpy data, the equations of enthalpy and heat capacity as temperature range of 298 ~ 1375 K were

$$H_T^0 - H_{298}^0 = 112.1T + 13.2 \times 10^{-3}T^2 + 1.47 \times 10^6 T^{-1} - 3.95 \times 10^4 \tag{13}$$

$$C_p = 112.1 + 26.4 \times 10^{-3}T - 1.46 \times 10^6 T^{-2} \tag{14}$$

respectively.

The resultant heat capacity of $ErMnO_3$ (Eq. (14)) is plotted in Fig. 6 with the results of DSC measurement (Eq. (12)), the MALT2 [13] and the results from the Neumann–

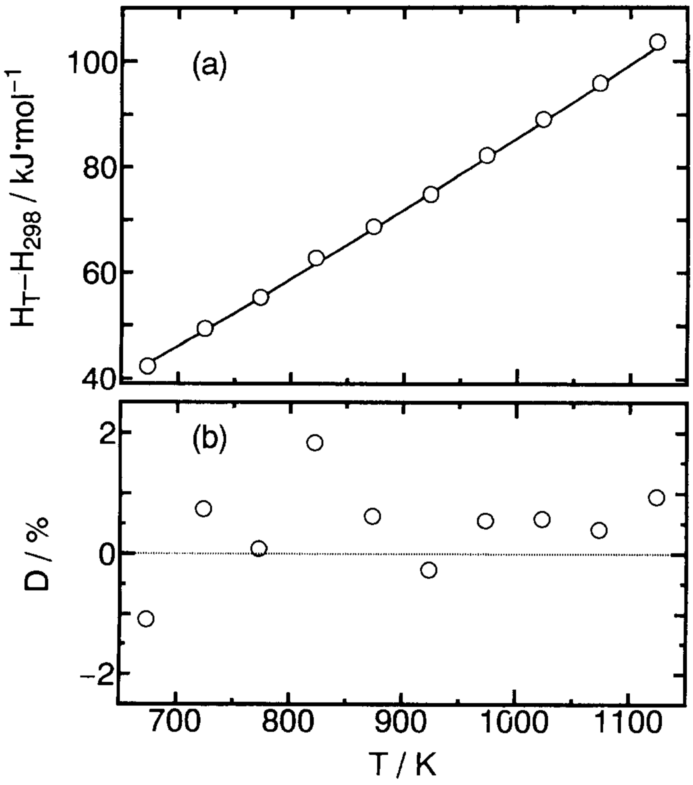

Fig. 3. (a) Enthalpies of Mn_2O_3: (———), the result of Orr [23]; ○, this study. (b) Relative deviation of this study from the result of Orr [23].

Kopp law which is the average of the heat capacities for Er_2O_3 and Mn_2O_3. From Fig. 6, the heat capacity obtained from the drop method is in good agreement with that from DSC, but in less agreement with the MALT2 and Neumann-Kopp law, especially at high temperature. Difference of the heat capacity between the result of drop method and MALT2 was about 11.1 J mol^{-1} K^{-1} or 8% at 1350 K. While the difference from Neumann-Kopp law was about 5.6 J mol^{-1} K^{-1} or 4%. This deviation will introduce error when the other thermodynamic properties are calculated.

Furthermore, the multiple regression analysis was carried out in order to unify the present two experiments by adopting the experimental values from DSC and from the drop methods in the temperature region of room temperature to 850 K and 673–1373 K predominantly, respectively. The revised equation in temperature range 298 ~ 1375 K is as follows

$$C_p = 111.9 + 26.4 \times 10^{-3} T - 1.33 \times 10^6 T^{-2} \qquad (15)$$

Similarly the revised equation for the enthalpy is as follows

$$H_T^0 - H_{298}^0 = 111.9T + 13.2 \times 10^{-3} T^2 + 1.33 \times 10^6 T^{-1} - 3.90 \times 10^4 \qquad (16)$$

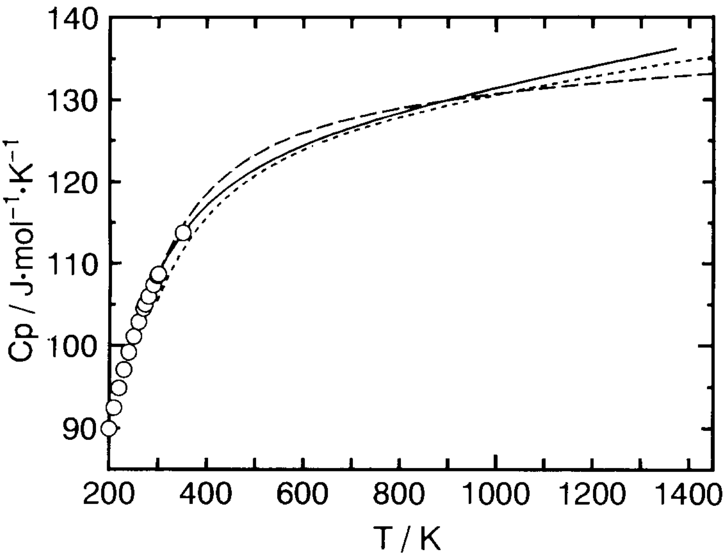

Fig. 4. Temperature dependence of the heat capacities of Er_2O_3: (– – –), Tsagareishvili and Gvelesiani [22]; (- - - -), Pankratz and King [21]; ○, Westrum Jr. and Justice [24]; (——), results observed from the present drop method.

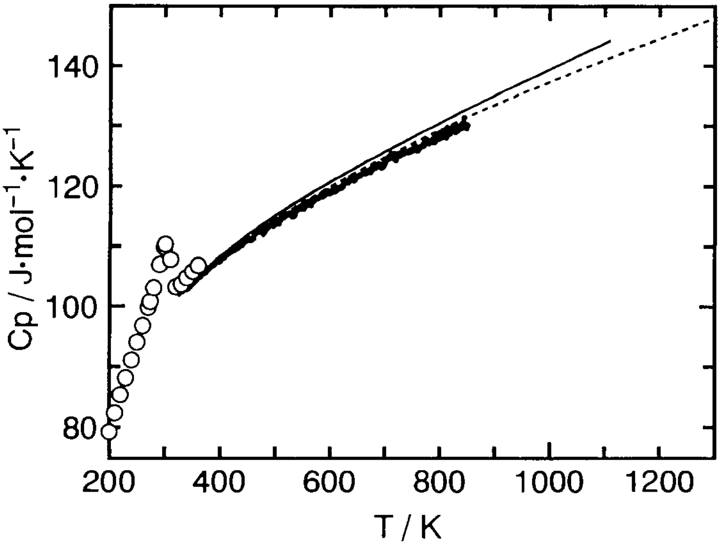

Fig. 5. Temperature dependence of the heat capacities of Mn_2O_3: (– – –) and ○, Robie and Hemingway [25]; (——), result observed from DSC method; and ●, result observed from the drop method.

Table 2
The observed enthalpy of $ErMnO_3$

T/K	$H_T^0 - H_{298}^0$/kJ mol^{-1}
673.5	43.44
721.4	49.78
771.3	56.83
822.1	64.44
875.1	70.07
921.3	77.27
980.4	84.26
1023.5	90.14
1073.1	98.11
1124.3	105.8
1174.3	111.9
1224.0	117.0
1272.8	125.1
1323.3	132.5
1374.9	140.8

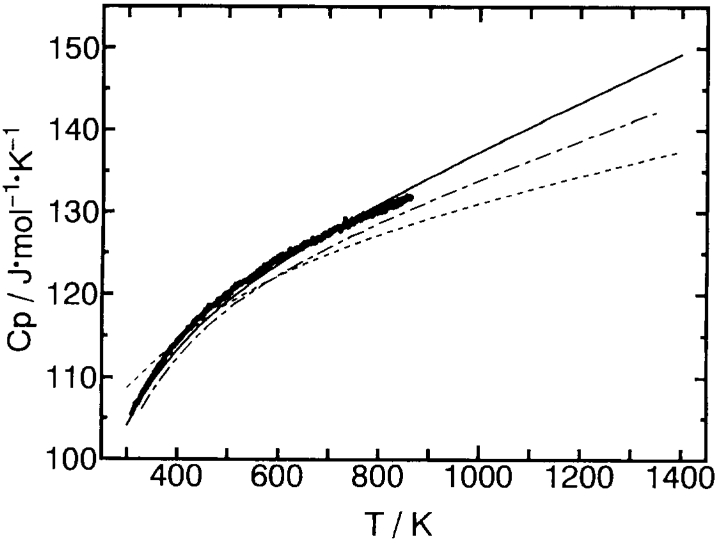

Fig. 6. Temperature dependence of the heat capacities of $ErMnO_3$: (– – –), value calculated by MALT2 [13]; (- - - -), calculated by the Neumann–Kopp law; (——), observed from the present drop method; and ●, result observed from the DSC method.

Using these equations, some other thermodynamic properties reported by Yokokawa et al. were modified. Kamata et al. [3] reported that the Gibbs free energy change of decomposition Eq. (1) at 1473 K was 11.2 kcal mol^{-1}. Hence, the Gibbs free energy change at 298 K was calculated from Eq. (8). $\Delta C_p = 1/2 C_p(Er_2O_3) + C_p(MnO) +$

Table 3
The smoothed heat capacity, enthalpy and entropy of $ErMnO_3$

T/K	C_p/ $J\,mol^{-1}\,K^{-1}$	$H^0_T - H^0_{298}$/ $kJ\,mol^{-1}$	$S^0_T - S^0_{298}$/ $J\,mol^{-1}\,K^{-1}$	$(G^0_T - H^0_{298})/T$/ $J\,mol^{-1}\,K^{-1}$	$\Delta G^0_{f,T}$/ $kJ\,mol^{-1}$
298	104.8	0.00	144.70	−144.70	−1362.73
300	105.0	0.19	145.40	−144.70	−1362.18
400	114.1	11.20	177.00	−148.96	−1335.51
500	119.8	22.91	203.11	−157.26	−1309.14
600	124.0	35.11	225.34	−166.80	−1283.05
700	127.7	47.70	244.74	−176.58	−1257.20
800	130.9	60.63	262.01	−186.20	−1231.55
900	134.0	73.88	277.61	−195.50	−1206.10
1000	137.0	87.43	291.88	−204.43	−1180.78
1100	139.8	101.3	305.07	−212.99	−1155.44
1200	142.7	115.4	317.36	−221.18	−1130.22
1300	145.4	129.8	328.89	−229.03	−1105.14
1400	148.2	144.5	339.77	−236.55	−1080.15

$1/4C_p(O_2) - C_p(ErMnO_3)$, where the heat capacities of Er_2O_3 [26, 19], MnO [26] and O_2 [26] were quoted from the literature. If the entropy of $ErMnO_3$ at 298 K is quoted from the value reported by Yokokawa et al. [12] ($\Delta S^0_{298} = 144.7\,J\,K^{-1}\,mol^{-1}$), the Gibbs free energy change of the decomposition reaction at 298 K can be calculated from Eq. (8). The result is 95.4 kJ mol^{-1}. On the other hand, since the standard Gibbs free energy of formation for Er_2O_3 [26] and MnO [26] are −1808.879 and −362.896 kJ mol^{-1}, respectively, the standard Gibbs free energy of formation for $ErMnO_3$ can be calculated from Eq. (9). The result is −1362.7 kJ mol^{-1}. Yokokawa et al. [12] reported that the standard Gibbs free energy of formation for $ErMnO_3$ is −1364.5 kJ·mol^{-1}. Difference between both energies was about 1.8 kJ·mol^{-1} (0.1%). This difference is the difference of the respective heat capacities such as described in Fig. 6.

Finally, C_p, $H^0_T - H^0_{298}$, S^0_T, and $G^0_{f,T}$ of $ErMnO_3$ are shown in Table 3. If the heat capacity of $ErMnO_3$ is measured below 298 K, more exact Gibbs free energies of formation will be derived.

4. Conclusion

Accuracy of the enthalpy measurements using the drop method was within ± 3%. Heat capacity of $ErMnO_3$ was measured by DSC and the drop methods, and both data were combined. Heat capacity yielded in this study has a few difference in comparison with the estimated values such as a part of MALT2 or the Neumann–Kopp law. The standard Gibbs free energy of formation for $ErMnO_3$ calculated with the combined heat capacity was larger than the reported value by 1.8 kJ mol^{-1}. The estimation in this case was in a fair agreement with the value of MALT2, but the entropy of $ErMnO_3$

at 298 K was used for the estimated value. Hence we need a further measurement of the heat capacity of $ErMnO_3$ at low temperature.

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