ELSEVIER

Thermochimica Acta 299 (1997) 123–126

thermochimica
acta

Heat capacity of $LaMnO_3$

Hirosia Satoh*, Masaki Takagi, Kei-ichi Kinukawa, Naoki Kamegashira

Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, Japan

Abstract

The heat capacity of $LaMnO_3$ was measured by differential scanning calorimetry (DSC) in the (150–760) K range and by alternative current calorimetry (ACC) in the (77–250) K range. The heat capacity curve showed two thermal anomalies due to a structural phase transition at 735 K and a magnetic transition at 140 K. The enthalpy and entropy changes accompanying the magnetic transition are 220 J mol^{-1} and 1.70 J $K^{-1}\cdot mol^{-1}$, whereas those for the higher temperature phase transition were estimated to be 3.36 kJ mol^{-1} and 4.2 J K^{-1} mol^{-1}. The non-transitional heat capacity of $LaMnO_3$ was calculated by multiple regression analysis and is given by the following expressions.

$$C_{p,m} = 2.82 + 0.874T - \frac{6.93 \times 10^4}{T^2} + 398 \times 10^{-7}T^3 - 3.31 \times 10^{-2}T^{3/2} \quad (77 \leq T \leq 298)$$

$$C_{p,m} = 96.73 + 5.36 \times 10^{-2}T - \frac{8.82 \times 10^5}{T^2} \quad (298 \leq T \leq 760)$$

Keywords: ACC; DSC; Heat capacity; $LaMnO_3$; Phase transition

1. Introduction

$LaMnO_3$ has an orthorhombically distorted perovskite-type structure at room temperature and undergoes a structural phase transition from the orthorhombic to the rhombohedral structure at high temperatures. The transition temperature depends on the oxygen non-stoichiometry [1]. A magnetic transition from anti-ferromagnetism to paramagnetism is observed near 140 K [2]. Also this transition temperature depend on the oxygen non-stoichiometry. The Gibbs free energy of decomposition or formation of $LaMnO_3$ has been reported by several authors [3–12]. The heat capacity and the derived thermodynamic properties above room temperature have been estimated by Yokokawa et al. [13,14]. No experimental heat-capacity data has however been published. We report the results of an experimental study of the heat capacity of $LaMnO_3$ in the (77–760) K range.

2. Experimental

$LaMnO_3$ was synthesized by a solid-state reaction method. Starting materials of La_2O_3 (Rare Metallic, Japan, of 99.99% purity) and Mn_2O_3 (Kojundo Chem. Lab., Japan, of 99.9% purity) were mixed in an equimolar ratio and pressed into a thin plate-shaped sample. The plate was sintered at 1523 K for 3 days under Ar flow. A single phase was identified by powder X-ray diffractometry and the lattice parameters were $a = 0.5739(1)$ nm, $b = 0.7698(1)$ nm $c = 0.5538(1)$ nm, respectively. These values were in good agreement with that reported by Norby

---

*Corresponding author.

PII S0040-6031(97)00147-0

et al. [15], i.e. $a = 0.57046(2)$, $b = 0.77029(4)$ and $c = 0.55353(3)$ nm. The degree of oxygen non-stoichiometry x in $LaMnO_{3+x}$ is below 0.01 in this preparation method [16].

Two types of calorimeter were used for the measurement of the heat capacity of $LaMnO_3$.; the DSC-220C and DSC-200 models of Seiko Electronic, Japan, were used for the (140–480) and (300–780) K temperature regions, respectively. ULVAC-2000 model ACC of Ulvac, Japan, was used in the (77–250) K temperature range. The accuracy of measurement with DSC was within ±1.5% at high temperatures, which was determined from the results of standard Al_2O_3. Since data yielded by ACC are relative values of the heat capacity, it is necessary to convert these relative values to the absolute values of heat capacity. A temperature-dependent calibration factor, X, was calculated from the temperature region which overlapped with the regions studied by the DSC method. The detailed procedures of the heat-capacity measurement with DSC and ACC are described in a previous paper [17–19].

3. Results and discussion

The heat capacity of $LaMnO_3$ is shown in Fig. 1 together with the values estimated by Yokokawa et al. [13]. In the heat capacity curve, two thermal anomalies corresponding to phase transitions were observed at 140 and 735 K, respectively. For the lower-temperature magnetic transition, the transition temperature of the present result is 140 K. The present work is in good agreement with the result by Matsumoto [2], which gave $T_{trans} = 141$ K.

The present work is in good agreement with that of Yokokawa et al. [14] at near room temperature. The agreement is not that good at higher temperatures. Differences between the values of Yokokawa et al. [14] and those of the present work are 3.5 J K^{-1} mol^{-1} at 600 K and 12.3 J K^{-1} mol^{-1} at 750 K, respectively. This is due to the fact that the heat capacity reported by Yokokawa et al. [13] was estimated by a modified Neumann–Kopp law. Furthermore, the transition temperature is 735 K in the present work, whereas 675 K is reported by Yokokawa et al. [13]. This difference is considered to be due to differences in oxygen non-stoichiometry of the specimens, as the transition temperature decreases with an increase of oxygen non-stoichiometry.

For the lower temperature transition, a base line shown as a solid line in Fig. 2 is obtained by multiple regression analysis. From the area between peak and the base line, the enthalpy and entropy changes accompanying the magnetic transition at 140 K are 220 J mol^{-1} and 1.70 J mol^{-1} K^{-1}, respectively. Corresponding enthalpy and entropy changes accompanying the structural transition at 735 K were calculated at 3.36 kJ mol^{-1} and 4.62 J mol^{-1} K^{-1}, respectively. Two non-transitional heat-capacity curves of $LaMnO_3$ were estimated by multiple regression analysis as

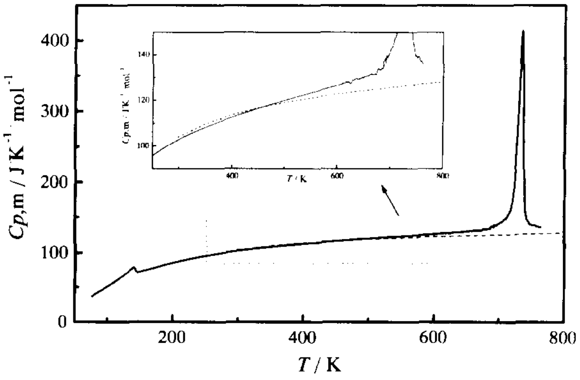

Fig. 1. The heat capacity of $LaMnO_3$. Solid and dashed lines indicate the present work and that of Yokokawa et al. [13], respectively.

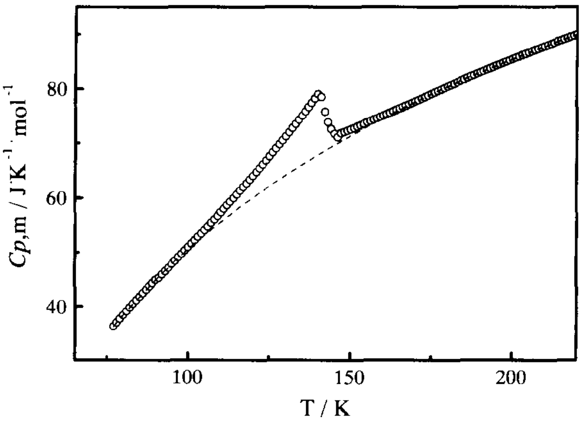

Fig. 2. The lower peak region of heat capacity of $LaMnO_3$. Circle and solid line indicate the observed value and the base line, respectively.

Table 1
Molar heat capacity of the two peak regions of $LaMnO_3$

$T/(K)$	$Cp,m/(J\ mol^{-1}\ K^{-1})$	$T/(K)$	$Cp,m/(J\ mol^{-1}\ K^{-1})$	$T/(K)$	$Cp,m/(J\ mol^{-1}\ K^{-1})$	$T/(K)$	$Cp,m/(J\ mol^{-1}\ K^{-1})$
100	50.92	138	77.39	665.15	131.13	728.15	274.03
105	54.08	139	78.18	670.15	131.88	729.15	295.95
110	57.31	140	78.98	675.15	133.69	730.15	319.74
112	58.63	141	78.48	680.15	133.58	731.15	343.25
114	59.96	142	75.76	685.15	134.07	732.15	364.06
116	61.31	143	73.84	690.15	137.78	733.15	385.27
118	62.67	144	72.56	695.15	138.72	734.15	405.40
120	64.05	146	71.09	700.15	141.67	735.15	413.76
122	65.45	148	72.06	705.15	144.25	736.15	373.99
124	66.87	150	72.54	710.15	147.71	737.15	271.46
126	68.31	152	73.03	712.15	150.66	738.15	196.12
128	69.77	154	73.53	714.15	154.34	739.15	166.08
130	71.25	156	74.04	716.15	158.34	740.15	154.95
132	72.75	158	74.54	718.15	163.58	741.15	149.58
134	74.27	160	75.05	720.15	172.32	742.15	147.01
135	75.04	165	76.34	721.15	178.11	744.15	144.41
136	75.82	170	77.64	722.15	185.16	746.15	141.13
137	76.60			723.15	194.02	748.15	139.62
				724.15	205.78	750.15	139.11
				725.15	220.28	755.15	138.70
				726.15	236.67	760.15	136.95
				727.15	254.39	764	136.19

shown in the following, and the smoothed molar heat capacity is tabulated in Table 1:

$$C_{\mathrm{p,m}} = 2.82 + 0.874T - \frac{6.93 \times 10^4}{T^2} + 398 \times 10^{-7}T^3 - 3.31 \times 10^{-2}T^{3/2} \quad (77 \leq T \leq 298)$$

$$C_{\mathrm{p,m}} = 96.73 + 5.36 \times 10^{-2}T - \frac{8.82 \times 10^5}{T^2} \quad (298 \leq T \leq 760)$$

The higher approximation of the Debye function is expressed by an equation such as

$$C_{\mathrm{v}} = 3nR\left(1 - \frac{\theta_{\mathrm{D}}^2}{20}\frac{1}{T^2}\right)$$

On the other hand, the temperature-dependence equation of the heat capacity is generally written as follow.

$$C_{\mathrm{p}} \equiv a + bT - \frac{c}{T^2} = a\left(1 - \frac{c}{a}\frac{1}{T^2}\right) + bT$$

Combining the coefficients of T^2 term from the two foregoing equations, the calculated Debye temperature 427 K was derived, in comparison with 460 K obtained from the heat capacity of $La_{0.8}Ca_{0.2}MnO_3$ from 110 to 300 K by Tamura and Kuriyama [20]. Comparing these two results, the estimated Debye temperature of $LaMnO_3$ (430 K) is a reasonably good derivation.

Acknowledgements

The authors thank Fuji Electrochemical Co., Ltd. for the availability of ACC apparatus. The present work was supported by a Grant-Aid for Scientific Research on Priority Areas "New Development of Rare-earth Complexes" No. 08220233 by the Ministry of Education, Science, Sports and Culture.

References

[1] A. Wold and R.J. Arnott, J. Phys. Chem. Solids, 9 (1959) 176.
[2] G. Matsumoto, IBM J. Res. Develop., 14 (1970) 258.
[3] K. Kamata, T. Nakajima, T. Hayashi and T. Nakamura, Mater. Res. Bull., 13 (1978) 49.
[4] T. Nakamura, G. Petzow and L.J. Gaucker, Mater. Res. Bull., 14 (1979) 649.
[5] Yu.P. Vorobev, A.A. Novlev, S.A. Leontev, A.N. Men, S.A. Prokudina and Y.S. Rubinchik, Iz. Akad. Nauk SSSR, Neorg. Mater., 15 (1979) 1449.
[6] O.M. Sreedharan, R. Pankajavalli and J.B. Gnanamoorthy, High Temp. Sci., 16 (1983) 251.
[7] M.L. Borlera and F. Abbattista, J. Less-Comm., Metals., 92 (1983) 55.
[8] N. Kamegashira, Y. Miyazaki and Y. Hiyoshi, Mat. Lett., 2 (1984) 194.
[9] V.A. Cherepanov, L.Y. Barkhatova and A.N. Petrov, J. Phys. Chem. Solids, 55 (1994) 229.
[10] J.A.M. van Roosmalen and E.H.P. Cordfunke, J. Solid State Chem., 110 (1994) 113.
[11] R. Hildrum, M. Brustad, W. Changzhen and O. Johnnesen, Mater. Res. Bull., 29 (1994) 851.
[12] T. Atsumi, T. Ohgushi and N. Kamegashira, J. Alloys Comp., 238 (1996) 35.
[13] H. Yokokawa, N. Sakai, T. Kawada and M. Dokiya, J. Am. Ceram. Soc., 73 (1990) 649.
[14] H. Yokokawa, N. Sakai, T. Kawada and M. Dokiya, J. Electrochem. Soc., 138 (1991) 2719.
[15] P. Norby, I.G. Krogh Andersen, E. Krogh Andersen and N.H. Andersen, J. Solid State Chem., 119 (1995) 191.
[16] N. Kamegashira, Y. Miyazaki and H. Yamamoto, Mater. Chem. Phys., 11 (1984) 187.
[17] H. Satoh, M. Horikawa and N. Kamegashira, J. Alloys Comp., 192 (1993) 99.
[18] H. Satoh, M. Horikawa and N. Kamegashira, Netsu Sokutei, 20 (1993) 193.
[19] H.W. Xu, J. Iwasaki, T. Shimizu, H. Satoh and N. Kamegashira, J. Alloys Comp., 221 (1995) 274.
[20] S. Tamura and M. Kuriyama, Phys. Lett., 70A (1979) 469.