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Heat capacities of (Ca,Ln)MnO_3 (Ln = Pr, Nd and Sm)

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Abstract

Heat capacities of $Ca_xLn_{1-x}MnO_3$ (Ln = Pr, Nd and Sm) for $x = 0.1$–0.6 were measured by using differential scanning calorimeter (DSC) and AC calorimeter (ACC). The thermal anomalies accompanied by magnetic transition from ferromagnetism to paramagnetism were observed within $x = 0.3$–0.6 and the transition temperatures, enthalpy and entropy changes were obtained. The magnetic contribution of heat capacity was estimated from a double exchange model. The estimated value was in a good agreement with the measured heat capacity.

Keywords: Perovskite; Heat capacity; DSC; ACC; Magnetic transition

1. Introduction

(A,Ln)MnO_3 (Ln = rare earth, A = alkali earth metals) has been studied on magnetic and electrical properties [1–5]. Knizek et al. [1] reported about structure and magnetic properties of $Pr_{1-x}Sr_xMnO_3$. According to them, the maximum transition temperature (297 K) from ferromagnetism to paramagnetism reached for $Pr_{0.6}Sr_{0.4}MnO_3$. On the other hand, the antiferromagnetic arrangement for $x = 0.5$ was realized below 160 K. Recently, the compounds including manganese element have been noted for very interesting properties to exhibit colossal magnetoresistance effect [6–10].

Although data of thermodynamic properties is inevitable for the discussion on the phase stability and the reactivity with the other compound, only a few thermodynamic properties for (A,Ln)MnO_3 have been reported [11–13]. The magnetic specific heat and Debye temperature of $(La_{0.8}Ca_{0.2})MnO_{3+y}$ using laser flash method was measured by Tamura and Kuriyama [11] and stoichiometric $(La_{0.8}Ca_{0.2})MnO_3$ had a thermal anomaly near 180 K. Tanaka and Mitsuhashi [12] attempted theoretical calculation of magnetic heat capacity for $(La_{0.8}Ca_{0.2})MnO_3$. Liebe et al. [13] reported about heat diffusivity of $La_{1-x}Ca_xMnO_3$.

2. Experimental

$Ca_xLn_{1-x}MnO_3$ compounds (Ln = Pr, Nd and Sm, $x = 0.1$–0.6) were synthesized by the usual ceramic method at 1523 K for 48 h in air. These compounds have perovskite structure of $GdFeO_3$ type from the identification by X-ray diffractometry. The crystal system and the lattice parameters of these compounds are shown in Table 1. About an oxygen nonstoichiometry of the present specimens, since an oxygen content of $Ca_xLa_{1-x}MnO_3$ compounds was almost 3, we expected that the present specimens were also the stoichiometry.

Heat capacity was measured by using DSC (Differential Scanning Calorimeter) from 140 to 470 K in Ar flow with a rate of 10 K/min and using AC calorimeter (ACC) from 80 to 280 K under the depressurized He atmosphere with a rate of 2 K/min. For the measurement of heat capacity, heat quantities of empty pan, reference (standard α-Al_2O_3) and the specimen were measured by using DSC, and heat capacity was calculated from shift quantities of these values. The measurement by ACC was carried out for a thin tabular specimen and then heat capacity was determined after calibrating using the values from DSC near room temperature. The precision of DSC and ACC measurements were 2.5 and 3.0%, respectively. The detailed procedure was described in the previous papers [14,15]. The spontaneous magnetization of these compounds were measured by SQUID from 4 to 300 K.

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Table 1
Lattice parameters of $Ca_xLn_{1-x}MnO_3$

x	Crystal system	a (nm)	b (nm)	c (nm)
$Ca_xPr_{1-x}MnO_3$				
0.1	Orthorhombic	0.5446(1)	0.5608(1)	0.7646(1)
0.2	Orthorhombic	0.5461(2)	0.5515(2)	0.7694(1)
0.3	Orthorhombic	0.5423(1)	0.5446(1)	0.7651(2)
0.4	Orthorhombic	0.5416(1)	0.5443(1)	0.7656(2)
0.5	Orthorhombic	0.5456(4)	0.5489(2)	0.7650(5)
0.6	Orthorhombic	0.5413(7)	0.5402(6)	0.7639(7)
$Ca_xNd_{1-x}MnO_3$				
0.1	Orthorhombic	0.5390(1)	0.5536(1)	0.7603(2)
0.2	Orthorhombic	0.5394(3)	0.5528(1)	0.7605(9)
0.3	Orthorhombic	0.5407(1)	0.5482(2)	0.7655(1)
0.4	Orthorhombic	0.5406(4)	0.5441(1)	0.7644(8)
0.5	Orthorhombic	0.5385(2)	0.5445(3)	0.7655(5)
0.6	Orthorhombic	0.5365(3)	0.5416(6)	0.7632(3)
$Ca_xSm_{1-x}MnO_3$				
0.1	Orthorhombic	0.5726(2)	0.5368(4)	0.7526(1)
0.2	Orthorhombic	0.5627(1)	0.5377(2)	0.7546(4)
0.3	Orthorhombic	0.5535(1)	0.5378(2)	0.7565(2)
0.4	Orthorhombic	0.5549(2)	0.5373(1)	0.7556(2)
0.5	Orthorhombic	0.5456(4)	0.5389(2)	0.7550(5)
0.6	Orthorhombic	0.5505(4)	0.5361(8)	0.7530(5)

3. Results and discussion

Results of heat capacity measurements for $Ca_xPr_{1-x}MnO_3$ from $x = 0.2$–0.5 are shown in Fig. 1. Thermal anomalies were observed for $x = 0.3$–0.5, no anomaly was seen in the case of $x = 0.2$. The observed thermal anomalies correspond to the magnetic transition from ferromagnetism to paramagnetism. The transition temperatures at the peak have a tendency to increase with increasing x. Base line was determined by the multi-regression analysis from the data of heat capacity excepted the peak area. The enthalpy changes for each composition are evaluated by integrating subtraction the base line from the data, the entropy changes was also evaluated using value divided the previous subtraction, ΔC_p, by temperature. The transition temperatures, enthalpy and entropy changes are shown in Table 2. The thermal anomaly for $x = 0.4$ has the maximum change in enthalpy and entropy. Similar tendency for transition temperature, enthalpy and entropy changes were obtained for Ln = Nd. In the case of Ln = Sm, the larger change occurs at $x = 0.5$.

Table 2
Transition temperatures, enthalpy and entropy changes of $Ca_xLn_{1-x}MnO_3$ (Ln = Pr, Nd and Sm)

	T_t (K)			ΔH ($J\,mol^{-1}$)			ΔS ($J\,mol^{-1}\,K^{-1}$)		
	Pr	Nd	Sm	Pr	Nd	Sm	Pr	Nd	Sm
$x = 0.3$	216	220	–	468	297	–	2.12	1.35	–
$x = 0.4$	245	247	275	598	488	368	2.45	1.98	1.34
$x = 0.5$	250	249	278	532	474	589	2.13	1.90	2.10
$x = 0.6$	–	265	–	–	469	–	–	1.80	–

Bars indicate no peak observed.

All compounds showed ferromagnetic behavior at low temperature from the results of SQUID measurement. From the results of X-ray diffractometry, $Ca_xLn_{1-x}MnO_3$ compounds have a perovskite structure where Ca^{2+} and Ln^{3+} ions are assumed to occupy A-site at random in the general formula ABO_3. Then there exist three possible magnetic super-exchange interactions, Mn^{4+}–O^{2-}–Mn^{4+}, Mn^{3+}–O^{2-}–Mn^{3+} and Mn^{3+}–O^{2-}–Mn^{4+} in these compounds. As Mn^{4+}–O^{2-}–Mn^{4+} and Mn^{3+}–O^{2-}–Mn^{3+} interactions are antiferromagnetic and Mn^{3+}–O^{2-}–Mn^{4+} interaction is ferromagnetic [16,17], ferromagnetism of these compounds is mainly caused by the Mn^{3+}–O^{2-}–Mn^{4+} interaction.

The variation of transition temperatures (T_t) with contents of solid solution x is shown in Fig. 2. From this figure, the transition temperatures increase with Ca content and $(Ca,Sm)MnO_3$ has higher transition temperature than $(Ca,Pr)MnO_3$ or $(Ca,Nd)MnO_3$ where these two compounds have almost same transition temperatures. The rise of the transition temperature was caused by increment of ferromagnetic interaction and simultaneous decrease of antiferromagnetic

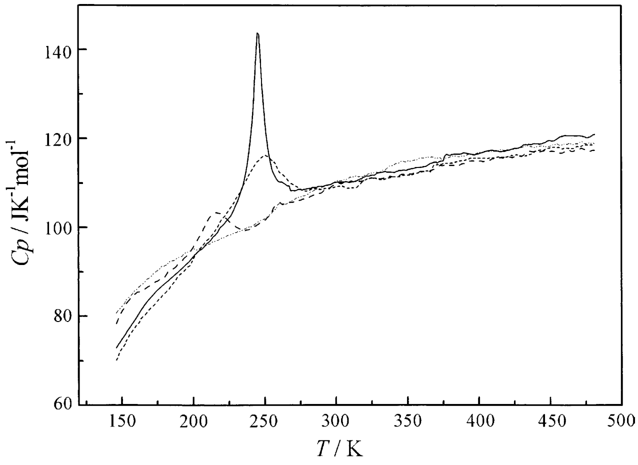

Fig. 1. Heat capacities of $Ca_xPr_{1-x}MnO_3$. Two-dotted broken line: $x = 0.2$; broken line: $x = 0.3$; solid line: $x = 0.4$; dotted line: $x = 0.5$.

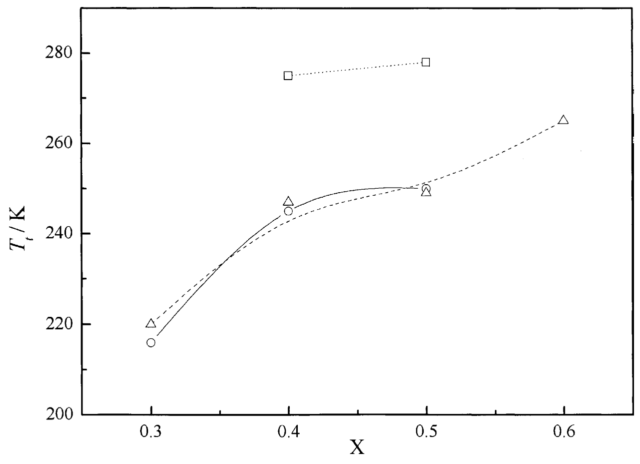

Fig. 2. Transition temperatures of $Ca_xLn_{1-x}MnO_3$. Circle: Ln = Pr; triangle: Ln = Nd; quadrangle: Ln = Sm.

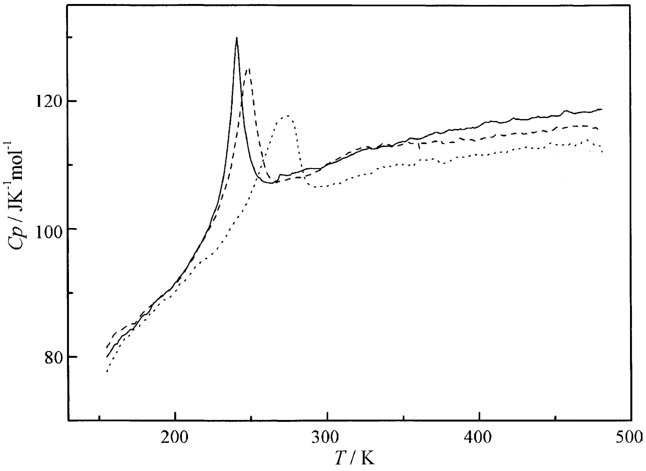

Fig. 3. Heat capacities of $Ca_{0.4}Ln_{0.6}MnO_3$. Solid line: Ln = La; broken line: Ln = Nd; dotted line: Ln = Sm.

interaction, because (Ca,Sm)MnO_3 structure has a greater distortion than other two compounds.

For the comparison of a fixed composition the heat capacities of $Ca_{0.4}Ln_{0.6}MnO_3$ (Ln = Pr, Nd and Sm) are shown in Fig. 3. The transition temperature increases in order for Ln = Pr, Nd and Sm, which will be expected from the previous described.

The magnetic contribution of heat capacity for these compounds was estimated from the value of the spontaneous magnetization by similar method by Tanaka and Mituhashi [13]. In this case the stabilization energy for the interaction is given as follows:

$$E = -NJzS^2\left(\frac{M}{M_0}\right)^2 \tag{1}$$

where N is Avogadro number, J a super-exchange interaction constant, z a coordinated number of Mn or Ni ion, S spin quantum number and M and M_0 are the spontaneous magnetization at any temperature and 0 K. A magnetic heat capacity, C_m, is derived to differentiate by temperature:

$$C_m = \frac{dE}{dT} = -NJzS^2\frac{d}{dT}\left(\frac{M}{M_0}\right)^2 \tag{2}$$

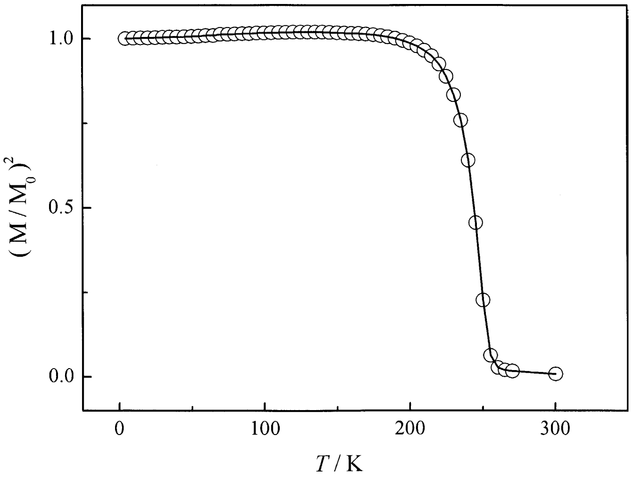

Fig. 4. Temperature dependence of the normalized magnetization for $Ca_{0.5}Sm_{0.5}MnO_3$.

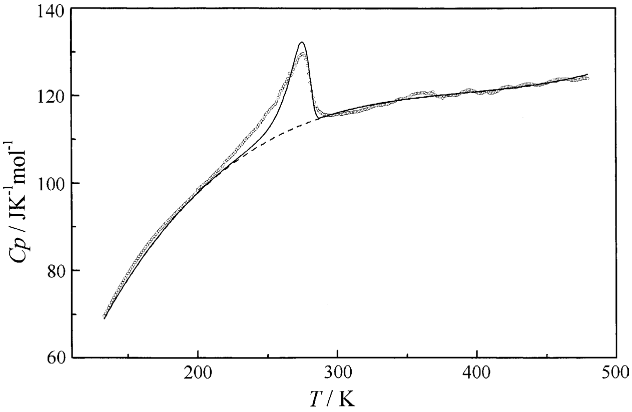

Fig. 5. Observed (circle) and estimated (broken line) heat capacities of $Ca_{0.5}Sm_{0.5}MnO_3$. Dotted line indicates the baseline.

The differential term could be calculated from the spontaneous magnetization of SQUID as is shown in Fig. 4. In Fig. 4, the normalized magnetization curve is expressed by a solid curve and then differentiation by temperature could be carried out. On the other hand, the difference of the stabilization energy between 0 K and any temperature T above the Curie temperature is simplified to $\Delta E = NJzS^2$ because $M_T/M_o = 0$ and $M_0/M_o = 1$, respectively. Since the constant term is able to regard as the enthalpy change, the magnetic heat capacity could be estimated. The results for $Ca_{0.5}Sm_{0.5}MnO_3$ are shown in Fig. 5. The estimated value is in a good agreement with the measured heat capacity. Therefore the observed thermal anomalies could be well explained by the magnetic transition from ferromagnetism to paramagnetism. For the compounds of other rare earths, similar results were obtained.

4. Summary

Heat capacities of $Ca_xLn_{1-x}MnO_3$ (Ln = Pr, Nd and Sm) were measured and the thermal anomalies were observed for several compositions. The magnetic contribution of heat capacity was estimated and in a good agreement with the measured heat capacity.

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