

BRIEF COMMUNICATIONS

High-Temperature Phase Transition of $\text{CaMnO}_{3-\delta}$

H. TAGUCHI* AND M. NAGAO

*Research Laboratory for Surface Science, Faculty of Science,
Okayama University, Okayama 700, Japan*

AND T. SATO AND M. SHIMADA

*Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Sendai 980, Japan*

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High-temperature phase transition of perovskite-type $\text{CaMnO}_{3-\delta}$ was examined by both thermal analysis (DTA) and high-temperature X-ray diffractometry. The crystal structure is orthorhombic below ca. 896°C, tetragonal between ca. 896 and 913°C, and cubic above ca. 913°C. © 1989 Academic Press, Inc.

CaMnO_3 has an orthorhombic perovskite-type structure and exhibits weak ferromagnetism with $T_N = 123$ K (1). A single crystal of CaMnO_3 was prepared by Poeppelmeier *et al.* (2) using a flux of CaO-CaCl_2 system. The space group of CaMnO_3 is $Pnma$, and the cell constants are $a = 0.5279$ nm, $b = 0.7448$ nm, and $c = 0.5264$ nm. Nonstoichiometric $\text{CaMnO}_{3-\delta}$ also exhibits antiferromagnetism (3), and is an n -type semiconductor (4).

$(\text{Ln}_{1-x}\text{Ca}_x)\text{MnO}_3$ (Ln : La and Nd), which is the substitution of Ca^{2+} ion by Ln^{3+} ion in CaMnO_3 , exhibits a metal-insulator transition without crystallographic change (5, 6); the mechanism of this transition is explained by the band model proposed by Goodenough (7). In the system $(\text{Ca}_{1-x}\text{La}_x)\text{MnO}_3$, the cell constants increase with in-

creasing x , and the crystal structure changes from orthorhombic to tetragonal symmetry at $x = 0.2$ (8). From the results of differential thermal analysis (DTA), the manganates with $x \leq 0.2$ gave endothermic peaks at ca. 890–915°C. On the other hand, the manganates with $x > 0.2$ did not give either exothermic or endothermic peak up to 1250°C (5).

In the present study, the crystal structure of $\text{CaMnO}_{3-\delta}$ is examined by high-temperature X-ray diffractometry above 900°C. These results provide some information regarding the relation between the crystal structure and endothermic peaks of DTA in $\text{CaMnO}_{3-\delta}$.

The preparation of $\text{CaMnO}_{3-\delta}$ was described in detail elsewhere (4). The sample was inserted into an alumina holder and heated at 10°C/min in a platinum heater, and kept more than 30 min at 900 or 920°C

* To whom all correspondence should be addressed.

TABLE I
CRYSTALLOGRAPHIC DATA OF CaMnO_{3-8}

Room temperature ($\text{CaMnO}_{2.98}$)				900°C ($\text{CaMnO}_{2.65}$)			
<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{cal.}	<i>I</i>	<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{cal.}	<i>I</i>
110	3.73	3.73	10	110)		3.77	
002	3.72	3.73	15	002)	3.77	3.77	15
111	3.33	3.33	2	111	3.37	3.37	2
200	2.642	2.641	45	200)		2.667	
112	2.636	2.636	100	112)		2.665	
020	2.633	2.633	95	020)	2.663	2.667	100
211	2.252	2.250	5	211)		2.274	
103	2.247	2.248	7	103)	2.275	2.272	2
202	2.155	2.155	5	202)		2.177	
022	2.150	2.150	5	022)	2.176	2.177	4
220	1.865	1.864	38	220	1.886	1.886	35
004	1.862	1.863	45	004	1.884	1.884	30
221)		1.809		221)		1.829	
203)	1.810	1.809	2	203)		1.828	
023	1.808	1.807	3	023)	1.829	1.828	5
310	1.670	1.670	5	310)		1.687	
222)		1.667		222)		1.686	
114)	1.667	1.667	7	114)	1.685	1.685	5
312	1.523	1.524	25	132)		1.539	
204	1.522	1.522	28	312)	1.540	1.539	35
024	1.521	1.521	33	204)		1.538	
132	1.520	1.520	33	024)	1.538	1.538	35
400	1.321	1.320	7	400)		1.333	
224	1.318	1.318	15	224)		1.332	
040	1.316	1.316	10	040)	1.333	1.333	15
420	1.180	1.180	7				
332	1.179	1.179	9				
116	1.178	1.178	12				
240	1.178	1.178	10				

$a = 0.5333 \text{ nm}$
 $c = 0.7534 \text{ nm}$

$a = 0.5282 \text{ nm}$
 $b = 0.5265 \text{ nm}$
 $c = 0.7452 \text{ nm}$

920°C
($\text{CaMnO}_{2.56}$)

<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{cal.}	<i>I</i>
100	3.76	3.77	10
110	2.667	2.669	100
111	2.177	2.179	5
200	1.887	1.887	45
210	1.688	1.688	15
211	1.541	1.541	45
220	1.335	1.335	15

$a = 0.3774 \text{ nm}$

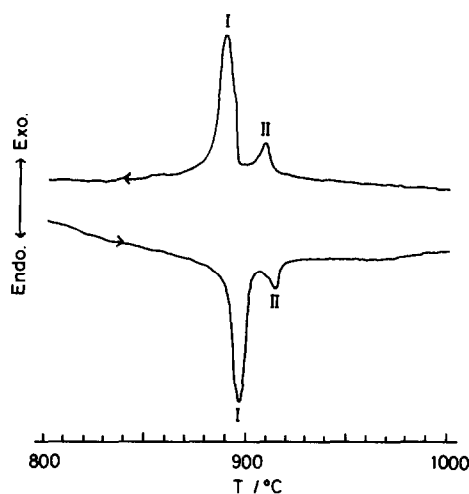


FIG. 1. DTA curve of $\text{CaMnO}_{3-\delta}$ measured at a rate of $10^\circ\text{C}/\text{min}$ in air.

in air. The temperature of the sample was monitored by an alumel–chromel thermocouple. Then, the phases of the sample were identified by X-ray powder diffraction with filtered $\text{CuK}\alpha$ radiation at prescribed temperature. Thermal analysis (DTA and TG) of the sample was performed in the temperature range from 20 to 1200°C in air.

Figure 1 shows the DTA curve of $\text{CaMnO}_{3-\delta}$ in the temperature range from 800 to 1000°C . The sample gave endothermic peaks at ca. 896°C (I) and 913°C (II) on heating, and exothermic peaks at ca. 908°C (II) and 890°C (I) on cooling, respectively. Below 880°C , the sample did not give either exothermic or endothermic peaks. From the results of TG, on heating, the weight of the sample gradually decreased with the appearance of the lower endothermic peak (I). On cooling, however, the weight of the sample gradually increased and became constant below the lower exothermic peak (I). The oxygen content of the sample at room temperature is determined to be ca. 2.98 from chemical analysis (6). The oxygen content of the sample at 900 and 920°C in air is ca 2.65 and 2.56, respectively.

These values were determined by TG after the sample was kept more than 30 min at the prescribed temperature.

X-ray powder diffractometry of the sample was measured at room temperature, 900 and 920°C . The observed and calculated interlayer spacings of the sample are shown in Table I. At room temperature, the X-ray diffraction patterns of the sample ($\text{CaMnO}_{2.98}$) were completely indexed as the orthorhombic perovskite-type structure. The cell constants are $a = 0.5282$ nm, $b = 0.5265$ nm, and $c = 0.7452$ nm, and these values nearly agreed with the values reported by Poeppelmeier *et al.* (2). At 900°C , the X-ray diffraction patterns of the sample ($\text{CaMnO}_{2.65}$) were completely indexed as the tetragonal perovskite-type structure with $a = 0.5333$ nm and $c = 0.7534$ nm. At 920°C , the number of the X-ray diffraction lines decreased and each peak became sharp. The X-ray diffraction patterns of the sample ($\text{CaMnO}_{2.56}$) were indexed as the cubic perovskite-type structure with $a = 0.3774$ nm. These results indicated that the relationship between cell constants among these phases were as follows: $a_{\text{tetra}} \approx \sqrt{2}a_{\text{cubic}}$ and $c_{\text{tetra}} \approx 2a_{\text{cubic}}$, $a_{\text{orth.}} \approx \sqrt{2}a_{\text{cubic}}$, $b_{\text{orth.}} \approx \sqrt{2}a_{\text{cubic}}$ and $c_{\text{orth.}} \approx 2a_{\text{cubic}}$.

From the results of the high-temperature X-ray diffractometry and thermal analysis, it is obvious that the endothermic or exothermic peaks (I and II) in DTA as shown in Fig. 1 correspond to the phase transition of $\text{CaMnO}_{3-\delta}$. On heating, the crystal structure is orthorhombic below the lower endothermic peak (I), tetragonal between the lower and higher endothermic peaks (I and II), and cubic above the higher endothermic peak (II).

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