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LATTICE CONSTANTS OF MONOCLINIC $(La_{0.8}Ca_{0.2})MnO_3$

Junzo TANAKA*, Koichiro TAKAHASHI, Yoshiyuki YAJIMA,
and Masayuki TSUKIOKA

National Institute for Research in Inorganic Materials,
Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki 305

The homogeneous sample of $(La_{0.8}Ca_{0.2})MnO_3$ was prepared by the coprecipitation method and its lattice constants were determined by X-ray powder diffraction to be a=c=7.759Å, b=7.745Å and β=90.3°. The homogeneity of the distribution of ions can be seen in the narrow half-widths of X-ray reflections.

Some studies on electrical conduction and magnetic properties of $(La_{1-x}Ca_x)MnO_3$ have been performed up to date; however, its conduction mechanism and origin of ferromagnetism have not been clarified.1 – 4) The difficulty of the studies on $(La_{1-x}Ca_x)MnO_3$ is partly due to the restriction of the variety of experimental data4) and partly due to the sample preparation: no single crystal with high quality has been grown,5) and no polycrystalline sample with homogeneous distribution of constituents has been synthesized so far. Homogeneity of the distribution of ions in many-component system, in general, sensitively influences its physical properties. A coprecipitation method6) is adopted here in order to obtain starting materials which are well-mixed, fine and reactive; such starting materials must result in the homogeneous distribution of main constituents in the final compound. The present letter reports the method of the synthesis and the result of X-ray powder diffraction of homogenous $(La_{0.8}Ca_{0.2})MnO_3$; the compound with x=0.2 most typically shows ferromagnetic and semiconductive behaviors in this series.4)

High-purity MnO_2(Rare Earth Ltd., 99.99%), La_2O_3 and $CaCO_3$(Shin-etsu Chemicals Co., 99.99%) were used as starting materials. MnO_2 was fired in flowing oxygen at 1200°C for 24h, being converted into Mn_3O_4, which is the most stoichiometric among manganese oxides. La_2O_3 was calcined in air at 1200°C for 6h to eliminate absorbed water. After these pre-treatments, the materials were weighed at the molar ratio of La/Ca/Mn=0.8/0.2/1.0 and dissolved in a 3N HCl solution in a polyethylene beaker. An excess amount of 3N Na_2CO_3 solution was rapidly added into the chloride solution; then, the precipitates in the forms of $MnCO_3$, $CaCO_3$ and $La_2(CO_3)_3$ were simultaneously obtained. After 15 to 20 times washing with cold distilled water, the precipitates were filtered, dried, and fired at 600°C for 1h. After cooling, the resultant material was mixed, fired again at 1000°C for 12h, re-mixed after cooling, and finally sintered in flowing oxygen at 1200°C for 24h into a disc pellet of 15mm in diameter and 3 to 4mm in thickness. The density of the sample sintered was as high as 97 to 98% of the value calculated from lattice constants.

The concentrations of the main components in the sample were determined by chemical analysis; the result is shown in Table 1, which indicates that the compound obtained has the chemical formula of $(La_{0.80_1}Ca_{0.20_7})Mn_{1.00}O_{3.0_7}$. This suggests that the La, Ca and Mn ions nearly perfectly precipitate from the solution. The Na ions of 0.28wt.% exist as main impurity, while the other impurities do not exist more than several tens ppm. (This sample is hereafter denoted as CP-20.)

Table 1. Chemical analysis of $(La_{0.8}Ca_{0.2})MnO_3$.

Ions	Wt. %	
La	49.6	(50.0)*
Ca	3.6	(3.7)*
Mn	24.5	(24.7)*
Na	0.28	(0.0)*

* Values calculated from the chemical formula, $(La_{0.8}Ca_{0.2})MnO_3$.

For comparison, the sample with the same components as CP-20 was synthesized also by an ordinary solid-phase reaction. The starting materials weighed were mixed mechanochemically with acetone for 1h, and fired in flowing oxygen at 1000°C for 12h. The processes of mixing and firing were repeated three times to ensure a uniform and single phase. The resultant material was pulverized carefully, and sintered under the same conditions as the case of CP-20. The density of the sample sintered was as high as 87 to 92% of the value calculated. (This sample is denoted as SR-20.)

The X-ray powder diffraction was measured at room temperature with Ni-filtered CuKα radiation for the ground samples, CP-20 and SR-20. The diffraction lines observed for CP-20 are shown in Table 2 together with those calculated by using the lattice constants determined below. Figure 1 shows two detailed diffraction profiles observed for CP-20 and SR-20 near $2\theta=40.3°$ and $58.3°$. The former reflection can be ascribed to (111) reflection of perovskite subcell and the latter to (211) reflection. The two peaks of CP-20 respectively split into two or three lines, however, such splitting is obscure for SR-20. The lattice constants of SR-20 were therefore approximately determined as $a=b=c=7.735Å$, which are consistent with the result reported by Tamura and Yamamoto.[7)] On the other hand, the case of CP-20 is slightly complicated. The reflection (111) of the perovskite subcell in CP-20 splits into two lines with the roughly same intensity; such splitting of (111) reflection takes place only in a monoclinic lattice with $a \sim b \sim c$, but never in the cubic one reported in the previous paper[2,7)] nor determined for SR-20. By the least square method using several intense reflections, the unit cell of CP-20 was in practice identified as monoclinic with lattice constants of $a=c=7.759Å$, $b=7.745Å$ and $\beta=90.3°$. This unit cell of CP-20 contains eight perovskite subcells, which is deduced from the existence of weak (021) and (113) reflections as shown in Table 2. The observed d's are indexed also in Table 2, which are in fairly good agreement with the d-values calculated by using the lattice constants determined.

Now, what causes the difference of the structure between CP-20 and SR-20? This is interpreted as follows. The half-widths Δ of the X-ray reflections in CP-20 are

Table 2.

H	K	L[a)]	h	k	l[b)]	d(obsd)	d(calcd)[c)]	I[d)]
1	0	0	0	0	2	3.88	3.880	9
			0	2	0	3.87	3.873	7
			0	2	1	3.46	3.465	1
1	1	0	-2	0	2	2.751	2.751	35
			0	2	2	2.740	2.741	100
			2	0	2	2.736	2.736	67
			-1	1	3	2.339	2.343	2
			-1	3	1		2.337	
			1	1	3		2.336	
			1	3	1		2.335	
1	1	1	-2	2	2	2.242	2.243	14
			2	2	2	2.234	2.235	10
2	0	0	0	0	4	1.940	1.940	27
			0	4	0	1.935	1.936	25
2	1	0	-2	0	4	1.733	1.739	3
			0	2	4		1.734	
			0	4	2		1.733	
			2	0	4		1.731	
2	1	1	-2	2	4	1.586	1.586	17
			-2	4	2	1.583	1.583	28
			4	2	2	1.580	1.581	14
			2	4	2		1.581	
2	2	0	-4	0	4	1.375	1.375	3
			0	4	4	1.370	1.370	13
			4	0	4	1.367	1.368	8
2 3	2 0	1 0	-4	2	4	1.295	1.296	1
			-2	4	4		1.294	
			0	0	6	1.292	1.293	2
			0	6	0		1.291	
			2	4	4		1.291	
			4	2	4		1.290	
3	1	0	-2	0	6	1.229	1.229	3
			0	2	6	1.226	1.227	7
			2	0	6	1.224	1.225	5
			0	6	2		1.225	
3	1	1	-2	2	6	1.169	1.171	2
			-2	6	2		1.169	
			2	2	6		1.168	
			2	6	2		1.167	
2	2	2	-4	4	4	1.122	1.121	2
			4	4	4	1.119	1.117	3

X-ray diffraction lines of $(La_{0.8}Ca_{0.2})MnO_3$.

a) Miller index of perovskite subcell.

b) Miller index of monoclinic cell containing eight perovskite subcells.

c) d-value calculated by a=c=7.759Å, b=7.745Å and β=90.3°.

d) Normalized intensity

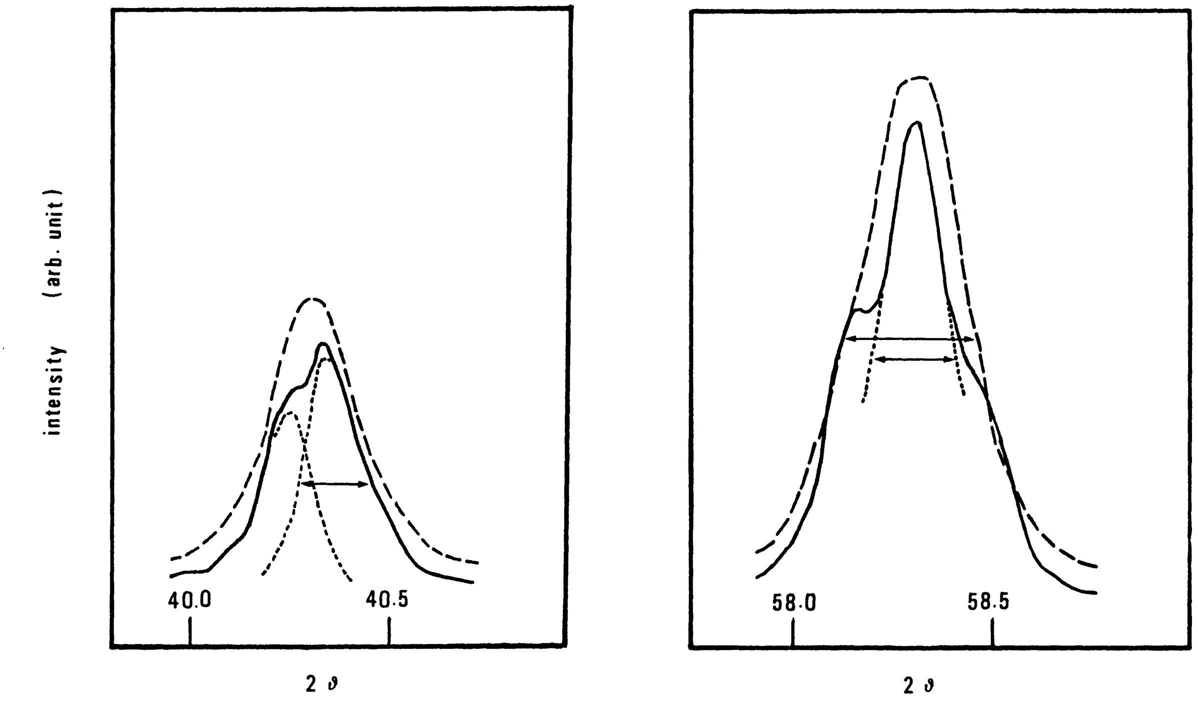

Fig.1. X-ray diffraction profiles of $(La_{0.8}Ca_{0.2})MnO_3$ with Cukα radiation; left: (111), right: (211). Solid lines show the results for the sample synthesized by the coprecipitation method, broken lines for the sample by the simple solid-phase reaction, and dotted lines for the resolved components of the solid lines. Arrows indicate the half-widths.

1/2 to 2/3 smaller than those in SR-20: Δ=0.18° in CP-20 and Δ=0.29°∿0.33° in SR-20. The half width Δ generally reflects inhomogeneity of the distribution of constituents or internal strains of materials, etc.[8)] Since the coprecipitation method, in principle, gives materials whose constituents are homogeneously distributed in atomistic order,[9)] it is considered that the narrow half-width of CP-20 reflects such homogeneity and that no splitting of the X-ray reflections in SR-20 probably results from the inhomogeneity of the distribution of ions, especially La^{3+} and Ca^{2+} ions. The crystal system of $(La_{0.8}Ca_{0.2})MnO_3$, therefore, cannot be essentially attributed to the cubic one but to the monoclinic one.

Magnetic properties and electrical conduction of homogeneous CP-20 are under investigation in relation to the origin of ferromagnetism; the homogeneity of the distribution of ions distinctly effects also the magnetic and electrical properties of CP-20 as well as the crystal system. The detailed magnetic properties and the effects of the homogeneity to physical properties will be published in the near future.

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