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A New Phase of Compound CaMnO$_{2+\delta}$ 1)

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Synopsis. A new phase of CaMnO$_{2+\delta}$ was synthesized by a wet process, followed by calcining. The structure was determined to be orthorhombic, with these lattice constants: a=5.96, b=14.38, and c=5.72 Å. Phase transformations among CaMnO$_{2+\delta}$ compounds were studied in various atmospheres, such as N$_2$, CO$_2$, and air.

Compounds of alkaline-earth oxide with transition metals have various crystal structures depending on whether there is an excess or deficiency of oxygen. The CaMnO$_{2+\delta}$ system was chosen in order to study systematically how the crystal structures of manganese oxides change with varied valences of Mn ions.

Mizutani *et al.*[2,3] reported that SrMnO$_3$ perovskite was transformed to Sr$_2$Mn$_2$O$_5$ brownmillerite-type compound, under N$_2$ atmospheres at 1500 °C. Since both Sr and Ca are alkaline-earth metals, a new phase with the composition of Ca$_2$Mn$_2$O$_5$ was expected to be synthesized.

Experimental

The synthesis of the compounds was carried out as follows. The reagents used were: CaCO$_3$ (alkaline metal analysis grade; Kanto Chemical Co., Inc.), Na$_2$CO$_3$ (reagent grade; Kanto Chemical Co., Inc.), and MnCO$_3$ (reagent grade; Wako Pure Chemical Industries Ltd.). A mixture of CaCO$_3$ and MnCO$_3$ in a molar ratio of 1:1 was dissolved into an HCl solution. An excess of an aqueous solution of Na$_2$CO$_3$ was added to the above solution to coprecipitate both Ca and Mn ions as carbonates in order to prepare a homogeneous materials; washing with distilled water followed to eliminate the Na ions thoroughly. The mixed precipitate was filtered, dried in air, and then calcined in an atmosphere with a volume ratio of H$_2$/Ar=1/3 at 900 °C for 2 h in a platinum crucible. Finally, the compound was heated again in the same atmosphere and at the same temperature for 17 h. The light green product was identified as a cubic (Ca, Mn)O solid solution by X-ray diffractometry. The composition of the solid solution was determined to be CaMn$_{1.01}$O$_{2.07}$ with 0.05 wt% of Na and 0.089 wt% of H$_2$O as minor constituents.

Results and Discussion

It is of much interest that a remarkable difference in the oxidation processes of the compound was observed, depending on the heating conditions. When the compound was oxidized in air at 600—610 °C, only one line with a considerable broadness was found in X-ray powder diffractometry, suggesting an amorphous phase[2] in the range of δ=0.74—0.91. When the solid solution was kept in air above 610 °C, however, CaMnO$_{3-\chi}$ perovskite[4] was obtained in the stable range of χ=0.00—0.17 in oxygen vacancies. On the other hand, the (Ca,Mn)O in high-temperature oxidation behaves quite differently from that in low-temperature oxidation.

Table 1. X-Ray powder diffraction lines of Ca$_2$Mn$_2$O$_5$

hkl	d_{obsd}/Å	d_{calcd}/Å	I/I_0
?(110)	5.99	(5.51)	14
?(101)	4.84	(4.13)	9
200	3.01	2.98	11
002	2.88	2.86	16
141	2.71	2.71	100
150	2.61	2.59	54
102	2.56	2.58	19
221	2.49	2.48	14
240	2.29	2.29	17
042	2.23	2.24	29
?	2.17	—	12
202	2.07	2.06	18
260	1.88	1.87	15
330	1.84	1.84	24
143	1.63	1.62	11
053	1.58	1.59	14
233 082	1.52	1.52	13
400	1.50	1.49	10
004	1.48	1.43	11
323	1.35	1.35	13

Orthorhombic, a=5.961, b=14.38, c=5.72 Å.

When the (Ca,Mn)O compound was kept at 1000 °C for 2 h in CO$_2$(P_{O_2}=2×10^{-4} atm) and then rapidly quenched to room temperature, a new phase appeared, with the d-values shown in Table 1. The phase is very stable, for it was hardly oxidized at all even when kept at 1000 °C for about 1 h in air. The oxidation process was examined using a high-temperature X-ray diffractometer. When the new phase was heated in air at a constant rate of 10 °C/min, the CaMnO$_3$ perovskite peaks appeared at about 1050 °C; this reaction was completed at 1200 °C. The perovskite was reduced to the new phase when held in N$_2$ gas (P_{O_2}=5×10^{-4} atm) at 1000 °C for 20 h; it was examined using a rapidly-quenched sample. The transition between the

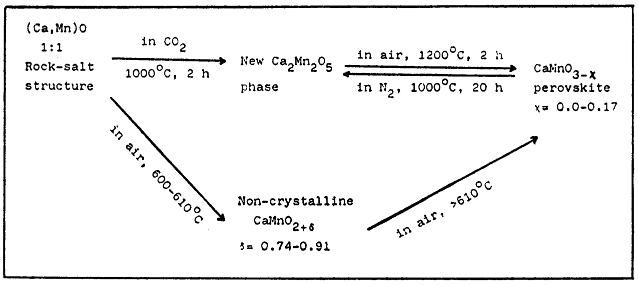

Fig. 1. Reaction diagram for CaMnO$_{2+\delta}$: (Ca, Mn)O solid solution, new Ca$_2$Mn$_2$O$_5$ phase and CaMnO$_3$ perovskite.

new phase and $CaMnO_3$ was reversible. These reaction processes are shown in Fig. 1.

Since the X-ray pattern in Table 1 is quite similar to that of orthorhombic $Sr_2Mn_2O_5$ (a brownmillerite-type compound), the new phase was identified as orthorhombic $Ca_2Mn_2O_5$ with the lattice constants of $a=5.96$, $b=14.38$, and $c=5.72$ Å, and with the axis ratios of $b/a=2.42$ and $c/a=0.96$. Using these values, the observed d_{obsd}'s are indexed in Table 1; they are in fair agreement with the calculated d_{calcd}'s except for a few lines. The chemical analysis of the new compound showed the composition of $CaMn_{1.01}O_{2.58}$.

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References

1) K. Takahashi, H. Yamamura, K. Muramatsu, and S. Shirasaki, Text of the Glass Division Meeting of the Ceramic Society of Japan, April, 1972.

2) N. Mizutani, Ph. D. Thesis, Tokyo Institute of Technology, Tokyo, Japan (1969).

3) N. Mizutani, N. Okuma, A. Kitazawa, and M. Kato, *Kogyo Kagaku Zasshi*, **73**, 1103 (1970).

4) W. O. Wollan and W. C. Koehler, *Phys. Rev.*, **100**, 545 (1955).