

Mn_{0.15}V_{0.3}Mo_{0.7}O₃, a New Compound in the MnV₂O₆–MoO₃ System

Jacek Ziólkowski,¹ Piotr Olszewski, and Bogna Napruszewska

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, 30-239 Kraków, Poland

Received December 27, 1996; in revised form February 3, 1998; accepted February 10, 1998

In the past we studied the system MnV₂O₆ (monoclinic, *C2/m*, brannerite-type structure)–orthorhombic MoO₃, including the MnΦ = Mn_{1-x}Φ_xV_{2-2x}Mo_{2x}O₆ solid solutions (Φ = cation vacancy in the original Mn site, X = 100x). MnΦ's isomorphous with the MnV₂O₆ matrix appeared to be stable upto X_{sat} = 42 at room temperature or at most X_{sat} = 45 at 520°C. Beyond these limits, MnΦ_{sat} and o-MoO₃ were observed to coexist. Now, a new phase Mn_{0.15}V_{0.3}Mo_{0.7}O₃ = Mn_{0.3}V_{0.6}Mo_{1.4}O₆ (or almost, referred to as the Y phase) has been identified in the MnV₂O₆–MoO₃ system at formal X = 70. It is monoclinic *P2/m* (*P2* or *Pm*) with *a* = 11.829(2) Å, *b* = 3.657(1) Å, *c* = 10.330(2) Å, β = 101.54(1)°, and *V* = 437.8(3) Å³. The Y phase prepared by a citrate precursor method starts to show reasonable (broadened) XRD reflections at 300°C, becomes predominant at 450°C, and decomposes slowly to MnΦ_{sat} and o-MoO₃ at higher temperatures (above 450°C). Apparently, due to the parallel course of the solid state reactions, an entirely pure Y phase has never been obtained. Samples with 65 ≤ X = 70 always contain some o-MoO₃ traces whereas those with 70 = X ≥ 80 are contaminated with MnΦ_{sat}. © 1998 Academic Press

1. INTRODUCTION

In our previous works (1–3) the defective brannerite-type phases have been described. Their monoclinic (most frequency *C2/m*) matrix is MeV₂O₆ (Me = Mg, Mn, Co, Cu, Zn). Isomorphous solid solutions are obtained on doping MeV₂O₆ with orthorhombic MoO₃ and/or monovalent *L* element oxides (*L* = Li, Na, Ag, K (4)). The general formula of these solid solutions is MeLΦ = Me_{1-x-y}Φ_xL_yV_{2-2x-y}Mo_{2x+y}O₆ (Φ = cation vacancy in the original Me/*L* site; X = 100x and Y = 100y).

The particular case of these studies is the system MnV₂O₆–o-MoO₃, comprising the MnΦ = Mn_{1-x}Φ_xV_{2-2x}Mo_{2x}O₆ solid solutions stable up to MnΦ_{sat} of X = 42 at room temperature or at most up to X = 45 at 520°C. Beyond these limits, the coexistence of MnΦ_{sat} and o-MoO₃ was observed (1).

On revising the MnV₂O₆–MoO₃ system, we discovered a new Y phase = Mn_{0.15}V_{0.3}Mo_{0.7}O₃ = Mn_{0.3}V_{0.6}Mo_{1.4}

O₆, formed at formal X = 70 and stable in the limited range of temperature 300 ≤ *T* ≤ 450°C. The aim of this work is to characterize this new Y phase.

2. EXPERIMENTAL AND TREATMENT OF DATA

The following samples, corresponding formally to the MnΦ_{1-x}V_{2-2x}Mo_{2x}O₆ system, have been considered/reconsidered: X = 0, 10, 20, 30, 40, 42, 50, 55, 60, 65, 70, 75, 80, 85, 90, 100 (series C = composition series).

All samples were synthesized by the amorphous citrate method (5) adapted empirically to the present system (2). Reactants were MnCO₃, NH₄VO₃, (NH₄)₆Mo₇O₂₄ · 4H₂O, 0.1 M ammonia, and citric acid, all of p.a. grade. The procedure has been described in ref 2. The final thermal treatment was carried in air at 520°C for 24–72 h, with grinding every 24 h; thereafter the samples were quenched.

Discovery of the new Y phase induced us to study an additional series of samples (series T = temperature series) of composition X = 70 but annealed at 300, 315, 325, 350, 400, 450, 500, 520, and 640°C for various times ranging from 24 to 200 h, with grinding every 24 h and pelleting in some cases.

X-ray diffraction patterns were obtained with a DRON-2 diffractometer using CuKα radiation; in some cases, an Al internal standard (*a* = 4.0492 Å at 25°C) was used. Data were collected on a floppy disk and processed with the SMOK (6) program for deconvolution and analysis of the spectra. Reflections in the range 5° < 2θ < 80° were used to determine the lattice constants. Further treatment of the data was performed with the following programs: PROSZKI (7) (involving, among others, DICVOL (8, 9), APPLEMAN (10), and LATCON (11)) and DBWS-9006 PC (12).

DTA was performed with a SETARAM M5 micro-analyzer (10°C/min, Pt crucibles, sample of about 12 mg, air atmosphere; treatment of DTA curves was described in ref 2).

3. RESULTS AND DISCUSSION

First, dealing with C-series samples, we noticed that close to X = 70, in addition to the reflections of MnΦ_{sat} and

¹To whom correspondence should be addressed.

TABLE 1

Phase Composition of Samples in the $\text{MnV}_2\text{O}_6\text{-MoO}_3$ System Formally Corresponding to the $\text{Mn}_{1-x}\Phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$ Formula ($X = 100x$) in the Temperature Range 300–520°C^a

X	Phase composition ^b
$0 \leq X \leq 42$	B
$42 < X \leq 60$	B + Y
$X = 65$	Y + traces of B and minor traces of o-M
$X = 70$	Y + minor traces of B and o-M
$X = 75$	Y + traces of o-M and minor traces of B
$X = 80$	Y + traces of o-M and minor traces of B
$80 < X < 100$	Y + o-M
$X = 100$	o-M

^a A very slow decomposition of Y is observed at 500 and 520°C; above 600°C the Y phase is melted and does not reappear on cooling.

^b B = brannerite ($\text{Mn}\Phi_{\text{sat}}$), Y = phase identified as $\text{Mn}_{0.15}\text{V}_{0.3}\text{Mo}_{0.7}\text{O}_3$, o-M = orthorhombic MoO_3 .

o- MoO_3 , seven distinct reflections appear which cannot be ascribed to any known phase. The unknown phase was preliminarily called the Y phase. A number of assays (Table 1) led us to the conclusion that the composition of the Y phase is most probably $\text{Mn}_{0.3}\text{V}_{0.6}\text{Mo}_{1.4}\text{O}_6 = \text{Mn}_{0.15}\text{V}_{0.3}\text{Mo}_{0.7}\text{O}_3$, although an entirely pure Y phase has never been obtained (also in the T series). The aforementioned seven reflections were analyzed with PROSZKI (7). A reasonable solution was found only for the monoclinic $P2/m$ ($P2$ or Pm) space group (no higher symmetry was found after further treatment of data). DICVOL gave about 20 solutions. Among them, we selected one satisfying the following requirements:

high figure of merit (above 60);

small volume of the unit cell (at most 500 \AA^3);

the shortest unit cell parameter, at least 3.6 \AA , which corresponds to the smallest, credible diagonal of the MoO_3 octahedron, believed to be the smallest motive of the structure.

The preliminary results (for seven reflections) smoothed by APPLEMAN and LATCON were about $a = 11.82 \text{ \AA}$, $b = 3.65 \text{ \AA}$, $c = 10.34 \text{ \AA}$, and $\beta = 101.3^\circ$. Further treatment consisted of calculating the reflection positions with DBWS (the latter program was used for an artificial phase to reach the entire list of $2\theta/hkl$, and to increase the number of considered reflections), and searching for the best fit with PROSZKI. At the end, we selected 26 reflections sufficiently free of overlap or noise. They gave $a = 11.825(2) \text{ \AA}$, $b = 3.654(1) \text{ \AA}$, $c = 10.328(2) \text{ \AA}$, and $\beta = 101.49(1)^\circ$.

At 300°C the T-series samples began to show some broadened XRD reflections that could be ascribed to the Y phase and $\text{Mn}\Phi_{\text{sat}}$. At 400°C the first reflections of o- MoO_3 appeared. This means that in spite of the "citrate mixing of reactants," parallel solid state reactions take place. In the range 350–450°C the time of annealing and

TABLE 2

Powder Diffraction Data for $\text{Mn}_{0.15}\text{V}_{0.3}\text{Mo}_{0.7}\text{O}_3$ (Monoclinic, $P2/m$, $a = 11.829(2) \text{ \AA}$, $b = 3.657(1) \text{ \AA}$, $c = 10.330(2) \text{ \AA}$, $\beta = 101.54(1)^\circ$; $V = 437.8(3) \text{ \AA}^3$)

k	l	h	$2\theta_{\text{obs}}$ (deg)	d_{obs} (\AA)	$2\theta_{\text{calc}}$ (deg)	d_{calc} (\AA)	I/I_0 (%)
1	0	0	7.64	11.581	7.628	11.589	6
-1	0	1	10.39	8.519	10.391	8.513	16
2	0	0	15.28	5.801	15.290	5.795	19
-2	0	1	16.06	5.521	16.032	5.528	10
-1	0	2	17.66	5.024	17.668	5.020	5
2	0	1	19.12	4.643	19.111	4.644	5
-2	0	2	20.89	4.254	20.870	4.256	5
-3	0	1	22.96	3.875	22.940	3.877	26
2	0	2	25.59	3.482	25.584	3.482	63
-1	0	3	26.01	3.427	25.993	3.428	100
1	1	1	27.54	3.240	27.551	3.237	19
-2	1	1	29.28	3.051	29.282	3.050	60
0	1	2	30.18	2.962	30.153	2.964	22
1	1	2	32.05	2.793	32.035	2.794	19
-4	0	2	32.40	2.764	32.390	2.764	24
3	1	0	33.76	2.655	33.750	2.656	12
-1	0	4	34.75	2.582	34.750	2.582	6
3	1	1	36.13	2.486	36.128	2.486	56
2	1	3	41.68	2.167	41.676	2.167	4
0	0	5	44.76	2.025	44.780	2.024	5
3	1	3	46.35	1.959	46.330	1.960	20
3	0	4	46.67	1.946	46.688	1.945	16
-5	1	2	46.85	1.939	46.843	1.939	6
5	1	1	48.87	1.864	48.853	1.864	11
6	0	1	49.82	1.831	49.798	1.831	41
-7	0	1	54.34	1.688	54.327	1.689	8
-4	1	5	55.91	1.645	55.914	1.644	23
-1	2	3	57.09	1.613	57.091	1.613	18
5	1	3	58.35	1.582	58.360	1.581	12
4	1	4	58.75	1.572	58.740	1.572	6
-1	1	6	59.44	1.555	59.421	1.555	18
-5	0	6	61.32	1.512	61.285	1.512	13
-2	1	7	68.69	1.367	68.671	1.367	10
-9	0	2	71.95	1.312	71.955	1.312	5

pelletting have no important influence on the XRD spectrum. At higher temperatures the Y phase slowly decomposes to $\text{Mn}\Phi_{\text{sat}}$ and o- MoO_3 . The Y phase never appeared after melting at 640°C. The most pure Y phase was obtained at 450°C after 110 h of annealing. Treating the XRD spectrum with the same procedure as described earlier, we have come to the conclusions gathered in Table 2, based on 34 reflections.

DTA of the sample treated at 450°C for 110 h showed a narrow endothermic doublet with an onset at 595°C, maxima at 607 and 615°C, and a satellite ending at 682°C. Taking into account that the sample was not equilibrated, it seems significant that the onset and ending temperatures coincide well with the eutectic melting and liquidus in the $\text{MnV}_2\text{O}_6\text{-MoO}_3$ system (1).

4. CONCLUSIONS

MnV_2O_6 (brannerite) and orthorhombic MoO_3 form a compound $\text{Mn}_{0.15}\text{V}_{0.3}\text{Mo}_{0.7}\text{O}_3 = \text{Mn}_{0.3}\text{V}_{0.6}\text{Mo}_{1.4}\text{O}_6$, appearing at 300°C and slowly decomposing above 450°C . The lattice constants of this monoclinic $P2/m$ ($P2$ or Pm) compound are $a = 11.829(2)\text{ \AA}$, $b = 3.657(1)\text{ \AA}$, $c = 10.330(2)\text{ \AA}$, $\beta = 101.54(1)^\circ$, and $V = 437.8(3)\text{ \AA}^3$.

REFERENCES

1. R. Kozłowski, J. Ziółkowski, K. Mocała, and J. Haber, *J. Solid State Chem.* **35**, 1 (1980) (erratum, *J. Solid State Chem.* **38**, 138 (1981)).
2. J. Ziółkowski, K. Krupa, and K. Mocała, *J. Solid State Chem.* **48**, 376 (1983).
3. B. Napruszewska, P. Olszewski, and J. Ziółkowski, *J. Solid State Chem.* **133**, 545 (1997), and papers quoted therein.
4. P. Olszewski, B. Napruszewska, and J. Ziółkowski, *J. Solid State Chem.*, in preparation.
5. P. Courty, H. Ajot, and C. Marcilly, *Powder Technol.* **7**, 21 (1973).
6. J. Wrzesiński, Elector Co., Kraków, Poland, 1992.
7. W. Łasocha and K. Lewiński, *J. Appl. Crystallogr.* **27**, 437 (1994).
8. D. Louer and M. Louer, *J. Appl. Crystallogr.* **5**, 271 (1972).
9. D. Louer and R. Vargas, *J. Appl. Crystallogr.* **15**, 582 (1982).
10. E. D. Appelman, H. T. Evans, and D. S. Handwerker, Program X-ray Geological, U.S. Department of the Interior, Washington, DC, 1966.
11. D. Schwarzenbach, Program for the Least-Squares Refinement of the Lattice Constants, Univ. of Lausanne, Switzerland, 1975.
12. A. Sakthivel and R. A. Young, School of Physics, GIT, Atlanta, GA, 1992.