CHEMISTRY LETTERS, pp. 21-24, 1973. Published by the Chemical Society of Japan

PREPARATION AND SOME PROPERTIES OF A NEW COMPOUND CONTAINING MoO_3, Al_2O_3 AND SiO_2

Akifumi UENO and Yoshihide KOTERA
National Chemical Laboratory for Industry

Mita, Meguro-ku, Tokyo

A new compound containing MoO_3, Al_2O_3 and SiO_2 was prepared by heating their mixture in a proper proportion at 1200°C for 12 hours. This compound was obtained in the form of small needle-like crystals, whose colour is slightly pale gray. Its composition was determined to be $\frac{1}{6}MoO_3 \cdot Al_2O_3 \cdot 2SiO_2$ by the chemical analysis. Crystallographic properties and preparative method of this compound were discussed in this report.

Introduction There have been no reports on the compound consisted of Al_2O_3, SiO_2 and MoO_3 so far. Some oxides other than Al_2O_3 or SiO_2 have been observed to form molybdates with MoO_3. For example, NiO[1] or FeO[2] was reported to react with MoO_3 and to form $NiMoO_4$ or $FeMoO_4$, respectively. With Bi_2O_3[3] MoO_3 forms $Bi_2Mo_2O_9$, $Bi_2(MoO_4)_3$, Bi_2MoO_6 and $3Bi_2O_3MoO_3$, while with PbO[4], it forms $PbMoO_4$ and Pb_2MoO_5. However, with Al_2O_3 or SiO_2 there have been few studies[5] probably because of their lower reactivities. The decomposition of Mo_5Si_3 in oxygen atmosphere was investigated to some extent[6], however, to form SiO_2 and MoO_3.

Molybdenum trioxide is volatile at above 800°C, therefore, only a few investigations[7] have been made on the intereaction of MoO_3 with other material at higher temperature. Moreover, no descriptions were found on their reaction at

above 1150°C, where MoO_3 begins to boil.

It would be interesting to know whether or not molybdenum trioxide reacts with the mixture of Al_2O_3 and SiO_2 at high temperature and forms a new compound containing them.

Experimental The starting materials are α-Al_2O_3, SiO_2 and MoO_3. Alpha alumina was obtained from Rigaku Denki Co. and was so pure as to be employed as the standard sample for D.T.A. and T.G.A.. Molybdenum trioxide obtained from Climax Molybdenum Co. contained less than 0.05% of metallic impurities. Silicon dioxide prepared by the hydrolysis of ethylsilicate and subsequent drying contained less than 0.01% of metallic impurities.

These oxides were well mixed after weighing of 2 gr. of α-Al_2O_3, 1 gr. of SiO_2 and 10-15 gr. of MoO_3. This mixture was put in a platinum crucible and covered with the excess of MoO_3. The crucible was placed in the electric furnace, whose temperature was gradually increased up to 1200°C and kept constant for 12 hours. Small needle-like crystals were formed on the inside wall of the crucible after gradual cooling to the room temperature. The colour of the crystal is slightly pale gray in an assembly, however each single crystal is transparent when observed under the microscope.

The X-ray crystallographic examination on a single crystal was carried out by using Weissenberg photograph and microphotometer. The density of the compound was obtained by the liquid displacement method using CCl_4, and the experimental error is within 5%. The composition of this product was determined by X-ray luminescence analysis and the chemical analysis. The infrared spectra were recorded on Jasco Model 403G grating spectrometer in the range of 1400-300 cm^{-1}. E.S.R. spectrometer (JES - 3BX type) was operated at 9400 MHz with 100 KHz modulation frequency.

Result and Discussion The crystal was determined to belong to the orthorhombic form with the mean lattice parameters; a=7.85A, b=7.63A and c=2.79A. The indexes and the intensities of the X-ray reflections are summarized in Table 1.

Weissenberg photograph of the single crystal showed that the diffraction symmetry was mmm, with systematic absences consistent

hkl	2θ	d	I/I₀	hkl	2θ	d	I/I₀
110	16.4	5.44	75.6	311	61.3	1.51	23.1
111	34.7	2.58	61.4	320	41.2	2.19	77.0
120	26.4	3.37	100.0	321	66.1	1.41	20.4
121	49.5	1.84	70.9	331	73.0	1.30	35.0
200	22.8	3.90	13.1	400	46.5	1.95	69.1
210	25.9	3.43	82.0	401	71.2	1.32	31.1
220	33.1	2.70	57.0	420	51.9	1.76	35.8
230	42.9	2.11	16.6	440	67.6	1.38	15.7
240	53.7	1.71	34.4	520	64.4	1.45	28.5
250	65.8	1.42	50.0	530	70.7	1.33	14.3
310	34.9	2.57	46.2				

Table 1 The indexes and the intensities of the X-ray reflections of the compound

with space groups P_{ba2}, P_{bam}, P_{na2_1}, and P_{nma}.

The components of this new compound were determined to be Al, Si and Mo by means of X-ray luminescence analysis, while its composition is estimated to be $\frac{1}{6}MoO_3 \cdot Al_2O_3 \cdot 2SiO_2$ by the chemical analysis. The measured density of the compound is 2.88 gr/cm^3 and the calculated ρ=2.45 gr/cm^3, Z=1 formula per unit cell.

The measurement of electric conductivity or magnetic susceptibility suggests that this new compound would be an insulate and diamagnetic substance. The amount of Mo(V) ion in this compound was estimated to be negligibly small by E.S.R. investigation and the result may be explained from the fact that this oxide would be diamagnetic.

The infrared spectrum of this compound was measured and compared with those of α-Al_2O_3, SiO_2 and MoO_3, as shown in Figs. 1 and 2. The absorption peaks at 1105, 810 and 465 cm^{-1} in Fig.1 are probably due to SiO_2 and they are in good agreement with those of SiO_2(Fig. 2). It is therefore considered that SiO_2 would exist in the tetrahedral form in this compound. MoO_3 and α-Al_2O_3 would exist in rather different form from octahedra, since some changes of their absorption spectra were observed in Fig. 1 against those of original materials in Fig. 2. There have been some investigations[8,9] on the difference of octahedral form (AlO_6) from tetrahedral one (AlO_4) by means of X-ray diffraction and infrared spectroscopy. According to the study[9], absorption peaks at 1160 and 730 cm^{-1} would be due to (AlO_4) species, and at peak 540 cm^{-1} due to (AlO_6) species; however, alumina would exist in this oxide in both forms of (AlO_6) and (AlO_4).

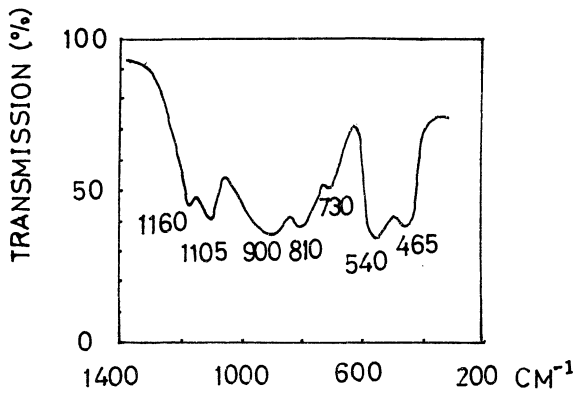

Figure 1 The infrared spectrum of the compound

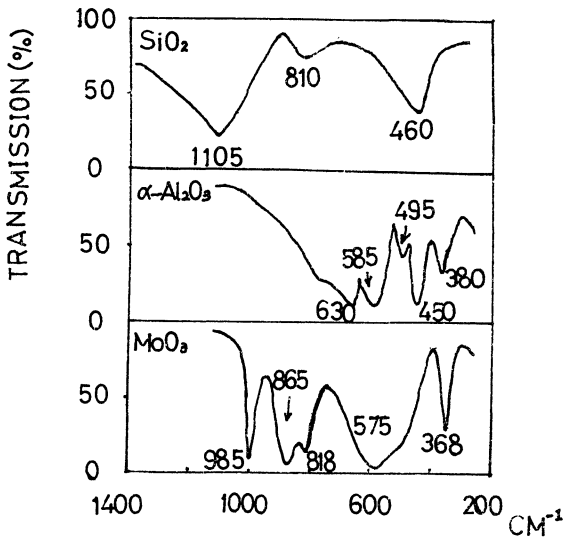

Figure 2 The infrared spectra of SiO_2, α-Al_2O_3 and MoO_3

The structure of this compound was not exactly investigated, therefore, it would be desirable to determine it in the near future.

Acknowledgment The authors express their thanks to Mrs. M. Goto and Mr. S. Shin in our Laboratory for their helpful discussions and encouragements.

References

1) J. A. Silvent, Rev. Nickel 27, 126 (1961).
2) Yu. D. Kozmanov and T. A. Ugolnikova, Zh. Neorg. Khim 3, 1267 (1958).
3) L. Ya. Erman, Russ. J. Inorg. Chem. 9, 1174 (1964).
4) I. N. Belyaev and N. P. Smolyaninov, Russ. J. Inorg. Chem. 7, 579 (1962).
5) T. Shirasaki, K. Morikawa et al., Catalysis (Shokubai) 4, 337 (1962).
6) J. H. Ashley and P. C. H. Mitchell, J. Chem. Soc., (A) 2821, 2730 (1968).
7) C. D. Wirkus and D. R. Wilder, J. Am. Ceram. Soc., 49, 173 (1966).
7) K. Nassau and J. W. Shiever, J. Am. Ceram. Soc., 52, 36 (1969).
V. K. Trumov, L. M. Kovba and E. I. Sirotkina, Dokl. Akad. Nauk SSSR 153, 1085 (1963).
8) D. E. Day and G. E. Rindone, J. Am. Ceram. Soc., 45, 489, 496, 576 (1962).
9) K. J. D. MacKenzie, J. Am. Ceram. Soc., 55, 68 (1972).

(Received November 14, 1972)