ACTA CHEMICA SCANDINAVICA 25 (1971) 2591–2595

Intermediary Phases in the Nb_2O_5—MoO_3 and Ta_2O_5—MoO_3 Systems

THOMMY EKSTRÖM

Institute of Inorganic and Physical Chemistry, University of Stockholm, Box 6801, S-113 86 Stockholm, Sweden

On specimens prepared within the temperature interval 640–900°C it was observed that intermediary phases $Nb_2O_5.3MoO_3$, $7Nb_2O_5.3MoO_3$, and $6Nb_2O_5.MoO_3$ were formed in the $Nb_2O_5-MoO_3$ system, and $\sim Ta_2O_5.3MoO_3$, $6Ta_2O_5.MoO_3$ in the $Ta_2O_5-MoO_3$ system. The phases have been characterized by their X-ray powder patterns, and unit cell dimensions for all, except $\sim Ta_2O_5.3MoO_3$, are given.

The $Nb_2O_5-MoO_3$ system has previously been investigated by Trunov *et al.*[1] For specimens prepared at 700°C, they reported the intermediary phases $Nb_2O_5.3MoO_3$, $2Nb_2O_5.MoO_3$ and $4Nb_2O_5.MoO_3$. In specimens heat-treated at 1100°C, only $4Nb_2O_5.MoO_3$ was found. More recently, Andersson[2] has reported two new phases $Mo_3Nb_{14}O_{44}$ ($7Nb_2O_5.3MoO_3$) and $MoNb_{12}O_{33}$ ($6Nb_2O_5.MoO_3$), formed by reaction of MoO_3 vapour with solid H-Nb_2O_5. In the $Ta_2O_5-MoO_3$ system, Kovba and Trunov[3] reported the presence of a phase $4Ta_2O_5.MoO_3$, and gave its unit cell parameters.

In this study, the $Nb_2O_5-MoO_3$ and $Ta_2O_5-MoO_3$ systems were investigated within the temperature interval 640–900°C, by heating appropriate amounts of Nb_2O_5 (Kawecki 99.99 %) or Ta_2O_5 (Koch-Light Lab. 99.9 %) with MoO_3 (Mallinckrodt 99.5 %). After thorough mixing, the specimens were heated in sealed silica tubes at reduced pressure (1/4 atm. at room temperature) for periods usually ranging from 1–7 days. After the heat-treatment, the silica tubes were quenched in cold water. All the specimens were investigated by recording their X-ray powder patterns in a Guinier-Hägg focusing camera with $CuK\alpha_1$ radiation, using potassium chloride (a = 6.29228 Å at 25°C) as an internal standard.

The $Nb_2O_5-MoO_3$ system

Series of samples $(Nb_xMo_{1-x})O_{3-0.5x}$ were prepared by heat-treatment at 640°, 750°, 800°, and 900°C (±5°C). The 640°C specimens did not reach equilibrium after heat-treatment for one week, and regrinding and heat-treatment for another week was necessary. The results of the X-ray powder phase analysis are given in Table 1. The intermediary phases $Nb_2O_5.3MoO_3$, $7Nb_2O_5.3MoO_3$, and $6Nb_2O_5.MoO_3$ were thus observed irrespective of the temperature applied in the preparation of the specimens.

Nb_2O_5. $3MoO_3$ ($Mo_3Nb_2O_{14}$). Trunov *et al.*[1] reported this phase to have a tetragonal unit cell with $a = 23.12 \pm 1$ Å, $c = 3.995 \pm 5$ Å. This is in concordance with the data obtained in the present study, $a = 23.13 \pm 1$ Å, $c = 4.000 \pm 2$ Å.

A comparison with the powder pattern of Mo_5O_{14} showed that the two substances are isostructural. According to Kihlborg,[4] the crystal structure of Mo_5O_{14} is built up in a complicated way by MoO_6 octahedra and MoO_7 pentagonal bipyramids. The binary oxide seems to be metastable at its temperature of formation. Partial substitution of several transition metals, including niobium, for molybdenum has been found to have a stabilizing effect on the structure. Results of studies on this matter will shortly appear elsewhere.[5]

$7Nb_2O_5.3MoO_3$ ($Mo_3Nb_{14}O_{44}$). This oxide is probably identical with the one reported by Trunov *et al.*[1] as $2Nb_2O_5.MoO_3$. They did not succeed to obtain this phase in pure state and gave the composition on the assumption that it was isostructural with a phase thought to be $2Nb_2O_5.WO_3$. The existence of this wolfram-niobium oxide has not been confirmed by later studies.[6,7] A comparison of the powder pattern obtained in the present study with the

Table 1. Experimental data for the system $Nb_2O_5 - MoO_3$, obtained from the X-ray diffraction patterns of specimens heat-treated at 640°, 750°, 800°, and 900°C. The brackets indicate traces of the phase concerned. The x-value corresponds to the formula $(Nb_xMo_{1-x})O_{3-0.5x}$.

Composition $x =$	Observed phases
0.20	$MoO_3 + Nb_2O_5.3MoO_3$
0.35	$(MoO_3) + Nb_2O_5.3MoO_3$
0.40	$Nb_2O_5.3MoO_3$
0.45	$Nb_2O_5.3MoO_3 + (7Nb_2O_5.3MoO_3)$
0.50	$Nb_2O_5.3MoO_3 + 7Nb_2O_5.3MoO_3$
0.75	$(Nb_2O_5.3MoO_3) + 7Nb_2O_5.3MoO_3$
0.80	$7Nb_2O_5.3MoO_3$
0.85	$7Nb_2O_5.3MoO_3 + (6Nb_2O_5.MoO_3)$
0.89	$7Nb_2O_5.3MoO_3 + 6Nb_2O_5.MoO_3$
0.92	$6Nb_2O_5.MoO_3$
0.95	$6Nb_2O_5.MoO_3 + Nb_2O_5$

pattern for $7Nb_2O_5.3WO_3$ reported by Roth and Wadsley[6] shows that the two oxides are isostructural. The lattice parameters for the tetragonal niobium-molybdenum oxide are $a = 21.024 \pm 5$ Å and $c = 3.818 \pm 2$ Å. Kovba and Trunov[8] have reported "$2Nb_2O_5.MoO_3$" to have the lattice parameters $a = 21.01 \pm 1$ Å and $c = 3.816 \pm 2$ Å. Recently, Andersson[2] has confirmed the existence of the $7Nb_2O_5.3MoO_3$ phase, and reports that this phase decomposes at ~ 950°C.

$6Nb_2O_5.MoO_3$ ($MoNb_{12}O_{33}$). It was not possible, in this study, to obtain single phase samples at the composition $4Nb_2O_5.MoO_3$ reported by Trunov *et al.*[1] (*cf.* Table 1 for $x=0.89$) as an intermediary phase. At this composition, a phase was observed with higher niobium content together with the $7Nb_2O_5.3MoO_3$ oxide. The observed phase was not satisfactorily indexed by the lattice parameters for the $4Nb_2O_5.MoO_3$ oxide given by Kòvba and Trunov.[3] Inspection of the powder patterns showed that the niobium-molybdenum oxide, obtained in this study, seems to be isostructural with $6Nb_2O_5.WO_3$.[6] The monoclinic unit cell has the lattice parameters $a=22.29\pm 2$ Å, $b=3.823\pm 2$ Å, $c=17.72\pm 2$ Å, and $\beta=123.4\pm 1°$. Andersson[2] has reported the $6Nb_2O_5.MoO_3$ oxide to be formed by reaction of MoO_3 vapour with solid H-Nb_2O_5.

The $Ta_2O_5-MoO_3$ system

Series of samples $(Ta_xMo_{1-x})O_{3-0.5x}$ were prepared by heat-treatment at 640°, 750°, 775°, 800°, 850°, and 900°C (±5°). The results of the phase analysis shows the intermediary phases $\sim Ta_2O_5.3MoO_3$ and $6Ta_2O_5.MoO_3$ to form within the investigated temperature interval. At the lowest preparation temperature, 640°C, no intermediary phase was observed, and at 900°C, none of the two phases had decomposed. The results of the X-ray powder phase analysis at 850°C are given in Table 2.

Table 2. Experimental data for the system $Ta_2O_5-MoO_3$, obtained from the X-ray diffraction patterns for the specimens heat-treated at 850°C. The brackets indicate traces of the phase concerned. The x-value corresponds to the formula $(Ta_xMo_{1-x})O_{3-0.5x}$.

Composition $x =$	Observed phases	
0.20	$MoO_3 + \sim Ta_2O_5.3MoO_3$	(melted)
0.35	$MoO_3 + \sim Ta_2O_5.3MoO_3$	
0.40	$\sim Ta_2O_5.3MoO_3$	
0.45	$\sim Ta_2O_5.3MoO_3$	
0.50	$\sim Ta_2O_5.3MoO_3 + (6Ta_2O_5.MoO_3)$	
0.80	$\sim Ta_2O_5.3MoO_3 + 6Ta_2O_5.MoO_3$	
0.85	$(\sim Ta_2O_5.3MoO_3) + 6Ta_2O_5.MoO_3$	
0.89	$6Ta_2O_5.MoO_3$	
0.92	$6Ta_2O_5.MoO_3$	
0.95	$6Ta_2O_5.MoO_3 + Ta_2O_5$	

$\sim Ta_2O_5.3MoO_3$ ($\sim Mo_3Ta_2O_{14}$). Within the temperature interval 640–675°C, a phase with the approximate composition $Ta_2O_5.3MoO_3$ was beginning to form. In Table 3, the X-ray powder pattern for the $\sim Ta_2O_5.3MoO_3$ oxide is given. It has not been satisfactorily indexed, and single crystals of sufficient size for Weissenberg photographs have not been obtained.

$6Ta_2O_5.MoO_3$ ($MoTa_{12}O_{33}$). At about 810°C, the phase $6Ta_2O_5.MoO_3$ was observed to form. A comparison with the powder patterns of $6Nb_2O_5.WO_3$

Table 3. X-Ray powder diffraction data for $\sim Ta_2O_5.3MoO_3$. $CuK\alpha_1$ radiation.

I	$\sin^2\theta_{obs.} \times 10^5$
m	842
m	2 589
w	3 371
vs	4 000
w	4 838
m	7 082
s	7 486
w	8 333
s	8 489
vw	10 369
m	11 484
m	11 868
w	12 327
w	13 479
w+	13 817
w	14 569
vw	15 087
s	15 984
w	17 567
s	18 967
m	20 978

and $6Nb_2O_5.MoO_3$ showed that the three substances are isostructural. The monoclinic unit cell of $6Ta_2O_5.MoO_3$ has the lattice parameters $a = 22.29 \pm 2$ Å, $b = 3.821 \pm 2$ Å, $c = 17.74 \pm 2$ Å, and $\beta = 123.4 \pm 1°$.

Kovba and Trunov [3] reported the presence of a phase $4Ta_2O_5.MoO_3$. The lattice parameters of the monoclinic unit cell of $4Ta_2O_5.MoO_3$ was calculated with the assumption that this phase was isostructural with a phase thought to be $4Nb_2O_5.MoO_3$. As mentioned above, the "$4Nb_2O_5.MoO_3$" phase seems to be the same as $6Nb_2O_5.MoO_3$, observed in the present study. The results thus obtained for "$4Ta_2O_5.MoO_3$" is not in concordance with the data obtained for $6Ta_2O_5.MoO_3$ phase in the present study.

GENERAL REMARKS

The $Nb_2O_5 - MoO_3$ system shows some similarities with the $Nb_2O_5 - WO_3$ system, where the isostructural phases $7Nb_2O_5.3WO_3$ and $6Nb_2O_5.WO_3$ have been reported by Roth and Wadsley [6] and Gruehn.[7] But the latter author suggested the $6Nb_2O_5.WO_3$ phase to have an extended homogeneity range to $8Nb_2O_5.WO_3$. No extended homogeneity range has, in the present study, been observed for $6Nb_2O_5.MoO_3$. The $7Nb_2O_5.3MoO_3$ and $6Nb_2O_5.MoO_3$ oxides can be characterized as shear or block compounds.

No phase isostructural to $Nb_2O_5.3MoO_3$ has been reported in the $Nb_2O_5 - WO_3$ system. In the area $Nb_2O_5.WO_3 - WO_3$, however, several phases exist,[9,10,11] which are related to the tetragonal potassium wolfram bronze type structure,[12] thus showing some similarities with the $Nb_2O_5.3MoO_3$ phase structure as having partially filled pentagonal tunnels with metal-oxygen running, parallel to the unique axes of the structures.

The phase relationships in the tantalum-rich area of the $Ta_2O_5-WO_3$ system are rather complicated [7,13] and thus differs from the $Ta_2O_5-MoO_3$ system, where only $6Ta_2O_5.MoO_3$ is observed. This phase is isostructural with the corresponding phases in the $Nb_2O_5-WO_3$ and $Nb_2O_5-MoO_3$ systems and can thus be characterized as a shear or block compound.

The powder pattern for $\sim Ta_2O_5.3MoO_3$ shows no similarities with any of the patterns observed in the $Nb_2O_5-MoO_3$, $Nb_2O_5-WO_3$ or $Ta_2O_5-WO_3$ systems. But in the corresponding compositional area of the latter systems, there exist phases that in some respects are related to the tetragonal wolfram bronze structure.

Acknowledgements. The author wishes to express his thanks to Professor Arne Magnéli and Drs. Lars Kihlborg and Mats Nygren for helpful discussions and their stimulating interest in this work.

The present study has been performed within a research program supported by the *Swedish Natural Science Research Council.*

REFERENCES

1. Trunov, V. K., Kovba, L. M. and Sirotkina, E. J. *Dokl. Akad. Nauk SSSR* **153** (1963) 1085.
2. Andersson, S. *Z. anorg. allgem. Chem.* **366** (1969) 96.
3. Kovba, L. M. and Trunov, V. K. *Vestn. Mosk. Univ. Ser. II Khim.* **19** (1964) 32.
4. Kihlborg, L. *Arkiv Kemi* **21** (1963) 427.
5. Ekström, T. and Nygren, M. *To be published.*
6. Roth, R. S. and Wadsley, A. D. *Acta Cryst.* **19** (1965) 26.
7. Gruehn, R. *Monatsh.* **96** (6) (1965) 115.
8. Kovba, L. M. and Trunov, V. K. *Zh. Strukt. Khim.* **6** (1965) 244.
9. Sleight, A. and Magnéli, A. *Acta Chem. Scand.* **18** (1964) 2007.
10. Sleight, A. *Acta Chem. Scand.* **20** (1966) 1102.
11. Stephenson, N. C. *Acta Cryst.* **B 24** (1968) 637.
12. Magnéli, A. *Arkiv Kemi* **1** (1949) 213.
13. Roth, R. S. and Stephenson, N. G. *Acta Cryst.* **A 25** (1969) 94.

Received December 21, 1970.