X-RAY DIFFRACTION STUDY OF DOUBLE OXIDES OF SOME TRANSITION METALS

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Abstract

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X-RAY DIFFRACTION STUDY OF DOUBLE OXIDES OF SOME TRANSITION METALS

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In the present work the formation of double oxides was investigated in the interaction of β-Nb_2O_5 with WO_3, MoO_3, V_2O_5 and of α-Ta_2O_5 with V_2O_5.

The investigation was carried out by us by the method of X-ray phase analysis. The samples were photographed in CuKα radiation in a focusing camera with a bent germanium single crystal as monochromator (^{1}). Annealing of mixtures of stoichiometric amounts of the initial oxides was carried out at temperatures from 700 to 1200°. Mixtures containing more than 80 mol.% WO_3 and all mixtures with MoO_3 were annealed in sealed quartz ampoules to prevent intensive evaporation of these oxides.

Table 1

X-ray phase analysis of samples in the β-Nb_2O_5—WO_3 system

WO_3, mol.%	Annealing conditions	Phase composition*
5	1200°	I
10	1200°	I+II
20	1200°	II
25—30	1200°	II+III
33.3	1200°	III
33.3	Melting	III
40—60	1200°	III+IV
62.5	1200°	IV+III (very little)
63.6	1200°	IV
66.7—73	1200°	IV+V
75	1100°	V
80	1100°	V+VI
85	1200°, sealed ampoule	V+VI+VII (very little)
90	1200°, sealed ampoule	The same
98	1200°, sealed ampoule	VI+VII (very little)

* I —solid solution of WO_3 in β-Nb_2O_5; II —$WO_3 \cdot 4Nb_2O_5$; III —$WO_3 \cdot 2Nb_2O_5$; IV —$7WO_3 \cdot 4Nb_2O_5$; V —$Nb_2O_5 \cdot 3WO_3$; VI —$Nb_2O_5 \cdot nWO_3$; VII —solid solution

of Nb_2O_5 in WO_3.

In the β-Nb_2O_5—WO_3 system we found the following compounds (Table 1): $WO_3 \cdot 4Nb_2O_5$ (20 mol.% WO_3), $WO_3 \cdot 2Nb_2O_5$ (33.3 mol.% WO_3), $7WO_3 \cdot 4Nb_2O_5$ (63.6 mol.% WO_3), $3WO_3 \cdot Nb_2O_5$, $Nb_2O_5 \cdot nWO_3$ (n 48–50).

In samples with a content of more than 90 mol.% WO_3, homogenization proceeds with difficulty, and on the X-ray diffraction patterns of all samples containing more than 90 mol.% WO_3, in addition to the lines of the $Nb_2O_5 \cdot nWO_3$ phase, there are present lines of WO_3 with a somewhat changed axial ratio, and in a number of samples also $3WO_3 \cdot Nb_2O_5$. The weakest lines of impurity phases are on the X-ray diffraction pattern of the sample with 98 mol.% WO_3; from the results of phase analysis it may be concluded that n 48–50. The $Nb_2O_5 \cdot nWO_3$ phase cannot be considered a solid solution of Nb_2O_5 in WO_3, since between WO_3 and $Nb_2O_5 \cdot nWO_3$ there exists a heterogeneous region, and the change in the WO_3 lattice on passing to $Nb_2O_5 \cdot nWO_3$ occurs discontinuously.

On the X-ray diffraction pattern of the phase $Nb_2O_5 \cdot nWO_3$ there is a large number of superstructure lines that are not observed for WO_3. The type of superstructure could not be established from the powder X-ray pattern.

The results obtained differ substantially from the data of Goldschmidt ([2]), who probably took the double oxides $WO_3 \cdot 4Nb_2O_5$ and $WO_3 \cdot 2Nb_2O_5$ to be a solid solution of WO_3 in β-Nb_2O_5, and the phases $7WO_3 \cdot 4Nb_2O_5$ and $3WO_3 \cdot Nb_2O_5$ to be a single compound. The phase $Nb_2O_5 \cdot nWO_3$ was apparently regarded by him as a solution of Nb_2O_5 in WO_3.

In the investigation of the system β-Nb_2O_5—MoO_3, the samples were annealed in sealed ampoules at temperatures of 700 and 1100° (see Table 2). In samples annealed at 1100°, only three phases are present: β-Nb_2O_5, MoO_3, and $4Nb_2O_5 \cdot MoO_3$, the X-ray pattern of which is identical with the X-ray pattern of $4Nb_2O_5 \cdot WO_3$. The sample with 20 mol. % MoO_3 contained only the phase $4Nb_2O_5 \cdot MoO_3$. We also carried out annealing of samples at 700°. On the X-ray patterns of samples with 66.7, 50, and 33.3 mol. % MoO_3, lines of three phases were present: MoO_3, $4Nb_2O_5 \cdot MoO_3$, and a phase isostructural with the compound $2Nb_2O_5 \cdot WO_3$. Homogenization of the sample with 33.3 mol. % MoO_3 proceeds with great difficulty (annealing at 800° for 14 days did not lead to homogenization of the sample), and therefore the phase $2Nb_2O_5 \cdot MoO_3$ could not be obtained in pure form; however, in view of the isostructurality of this phase with the phase $2Nb_2O_5 \cdot WO_3$, it may be considered that its composition is expressed by the indicated formula. The sample with 75 mol. % MoO_3 contained only the phase $Nb_2O_5 \cdot 3MoO_3$, the X-ray pattern of which proved not to be identical with the X-ray pattern of $Nb_2O_5 \cdot 3WO_3$.

Table 2

X-ray phase analysis of samples in the system β-Nb_2O_5—MoO_3*

Mol. % MoO_3	Annealing temp.**, °C	Phase composition
10	1100	I+II
20	1100	II
33.3–66.7	1100	II+III
75	1100	II+III+IV (very little)
90	1100	II (very little)+III
10	700	I+V
20	700	II
33.3	700	II+V+III (very little)
50	700	II+V+III (little)+IV
66.7	700	IV+V
75	700	IV
90	700	IV+III

* I –β-Nb_2O_5; II –$4Nb_2O_5 \cdot MoO_3$; III –MoO_3; IV –$3MoO_3 \cdot Nb_2O_5$; V – $2Nb_2O_5 \cdot MoO_3$.
** The samples were annealed in sealed quartz ampoules.

The structures of the oxides $7WO_3 \cdot 4Nb_2O_5$ and $3MoO_3 \cdot Nb_2O_5$, as well as the structure of $3WO_3 \cdot Nb_2O_5$, are probably built on the basis of the ReO_3 structure, with the difference that the double oxides $3WO_3 \cdot Nb_2O_5$ and $7WO_3 \cdot 4Nb_2O_5$ have a similar superstructure, from which the superstructure of $3MoO_3 \cdot Nb_2O_5$ differs considerably. All lines of the X-ray pattern of $3WO_3 \cdot Nb_2O_5$ (^{3}) and most lines of the X-ray pattern of $7WO_3 \cdot 4Nb_2O_5$ are indexed assuming a tetragonal unit cell, the c axis of which is analogous to the lattice period of ReO_3, while the a axis is the lattice period of ReO_3 increased by $\sqrt{10}$ times (i.e., corresponds to the 310 direction of the ReO_3 cell).

A certain number of weak lines of the X-ray pattern of the compound $7WO_3 \cdot 4Nb_2O_5$ are not indexed assuming a unit cell with such identity periods; the cell is rhombic, pseudotetragonal. If the cell period of ReO_3 is denoted by a', then the cell periods of $7WO_3 \cdot 4Nb_2O_5$ are: $a \approx a'\sqrt{10}$; $b \approx 3a'\sqrt{10}$ and $c \approx a'$, i.e. $a = 12.219 \pm 0.006$ Å; $b = 36.66 \pm 0.02$ Å and $c = 3.940 \pm 0.002$ Å.

The lines of the X-ray pattern of the compound $3MoO_3 \cdot Nb_2O_5$ are indexed assuming a tetragonal unit cell, the c axis of which is equal to the period a of the ReO_3 cell, while the direction of the a axis is apparently close to the 210 direction of the ReO_3 cell ($a = 23.12 \pm 0.01$ Å; $c = 3.995 \pm 0.005$ Å;

$z = 9$). The results of indexing the X-ray diffraction pattern of $3MoO_3 \cdot Nb_2O_5$ are given in Table 3.

Table 3

Results of indexing the X-ray diffraction pattern of $3MoO_3 \cdot Nb_2O_5$

I	d, kX	$1/d^2 \cdot 10^4$, found	$1/d^2 \cdot 10^4$, calculated	hkl	I	d, kX	$1/d^2 \cdot 10^4$, found	$1/d^2 \cdot 10^4$, calculated	hkl
4	11.5	75.5	75.4	200	2	3.257	943	942	710, 550
4	10.3	93.9	94.2	210	2	3.195	980	980	640
2	7.28	189	188	310	1	3.166	998	999	720
1/2	6.41	243	245	320	1/2	3.025	1093	1093	730
2	5.75	302	302	400	1/2	2.882	1204	1206	800
1/2	5.61	318	320	410	6	2.858	1224	1225	810
3	5.42	340	339	330	1/2	2.792	1283	1281	820
1/2	5.15	377	377	420	1	2.767	1306	1307	601
1/2	4.521	489	490	510	5	2.672	1401	1394	750
1/2	4.279	546	546	520				1402	541
1/2	4.076	602	603	440	1/2	2.604	1475	1478	631
10	3.989	628	629	001	1/2	2.523	1571	1572	711
4	3.842	678	679	600	1/2	2.494	1608	1610	641
1/2	3.794	695	697	610	1/2	2.478	1629	1628	721
1/2	3.712	726	724	211	1/2	2.341	1825	1828	940
1/2	3.646	754	754	620	3	2.323	1853	1855	811
7	3.599	772	772	540	1/2	2.290	1907	1904, 1911	10.1.0, 821
1/2	3.494	819	818	311	1/2	2.224	2022	2024	751
2	3.433	848	848	630					

In the absence of appreciable displacement of atoms from the subcell nodes, the 630 line of $3MoO_2 \cdot Nb_2O_5$ should have been the brightest among the $hk0$ lines. Such a regularity in the intensities of $hk0$ reflections is indeed observed for the oxides $3WO_3 \cdot Nb_2O_5$, $7WO_3 \cdot 4Nb_2O_5$, and $3WO_3 \cdot Ta_2O_5$. In the case of $3MoO_3 \cdot Nb_2O_5$, the brightest line is 540, which indicates a more considerable displacement of metal atoms from the subcell nodes than in the analogous tungsten compounds.

Table 4

Interplanar spacings for the phase $Nb_2O_5 \cdot nWO_3$

I	d, kX	I	d, kX	I	d, kX	I	d, kX
8	3.823	7	2.628	2	1.974	1	1.7816
10	3.691	2	2.581	4	1.9101	2	1.7090
1	3.241	1	2.194	6	1.8431	1	1.6822
3	3.070	4	2.138	1	1.8121	3	1.6592

I	d, kX	I	d, kX	I	d, kX	I	d, kX
6	2.678	1	2.015	4	1.7927		

The bright lines of the X-ray diffraction pattern of the $Nb_2O_5 \cdot nWO_3$ phase are indexed on the assumption of a monoclinic subcell with $a = 5.277$ Å, $b = 5.172$ Å, $c = 3.832$ Å, $\beta = 87°50'$. The presence of superstructure lines indicates an ordered arrangement of Nb and W atoms. The interplanar spacings for the $Nb_2O_5 \cdot nWO_3$ phase are given in Table 4.

In the systems β-Nb_2O_5—V_2O_5 and α-Ta_2O_5—V_2O_5, we established the existence of isostructural compounds $V_2O_5 \cdot 6Me_2O_5$ (14.3% V_2O_5) or $3V_2O_5 \cdot 17Me_2O_5$ (15 mol.% V_2O_5), where Me = Nb or Ta. All samples with other compositions (10, 20, 50, 90% V_2O_5) are two-phase, and their X-ray diffraction patterns contained lines of the starting oxides present in excess. The oxide $V_2O_5 \cdot 6Nb_2O_5$ corresponds to the β'-$(Nb, V)_2O_5$ phase found by Goldschmidt, who assigns to it a homogeneity range of 10–25 mol.% V_2O_5. According to our data, the phases $V_2O_5 \cdot 6Me_2O_5$ have a very narrow homogeneity range.

The present work practically completes the investigation of binary systems formed from the pentoxides of vanadium, niobium, and tantalum and the trioxides of molybdenum, tungsten, and uranium. Although the structures of these compounds have not been sufficiently studied, even the available data make it possible to divide these compounds into several groups. Uranyl vanadates, molybdates, and tungstates have a complex structure and are probably uranyl salts. The oxides $UMeO_5$ and $UMeO_{5+x}$ $(Me = V, Nb, Ta, Mo, W)$ and UMe_3O_{10}—UMe_3O_{10+y} $(Me = V, Nb, Ta)$ are built on the basis of the structure of α-UO_3—U_3O_8 and the α modifications of niobium and tantalum pentoxides. The ordered arrangement of metal atoms leads to the appearance of various superstructures. Several compounds ($Nb_2O_5 \cdot nWO_3$, $Nb_2O_5 \cdot 3WO_3$, $Nb_2O_5 \cdot 3MoO_3$, $Ta_2O_5 \cdot 3WO_3$, $7WO_3 \cdot 4Nb_2O_5$) are built on the basis of the ReO_3 structure. The ordered placement of metal atoms at the nodes of a primitive pseudocubic lattice, displacement of atoms from these ideal positions associated with deviations of the compositions from MeO_3, and distortion of the oxygen octahedra around the metal atoms lead to the appearance of superstructures. The Debye patterns of the compounds $V_2O_5 \cdot 6Me_2O_5$ $(Me = Nb, Ta)$, $4Nb_2O_5 \cdot MeO_3$, $2Nb_2O_5 \cdot MeO_3$ $(Me = W, Mo)$ somewhat resemble the Debye pattern of β-Nb_2O_5. Their structures can probably be regarded as intermediate between β-Nb_2O_5 and oxides built on the basis of the ReO_3 structure. All three latter groups of compounds are characteristic representatives of double oxides.

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Note: Figure translations are in progress. See original paper for figures.

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