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Studies on Rutile-Type Phases in Mixed Transition Metal Dioxides II *

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Rutile-type phases have been found to exist over wide ranges of composition in the systems TiO_2-NbO_2, TiO_2-MoO_2, NbO_2-CrO_2, and NbO_2-MoO_2. The phases show short metal-metal distances which are reflected in the low values of the axial ratio c/a. The relation to the concentration of valence electrons not engaged in metal-oxygen bonding is discussed.

It has previously been shown that remarkably short metal-metal distances exist in several dioxides of transition metals. This is the case for the dioxides of MoO_2 type, for the orthorhombic modification of rhenium dioxide and for rutile type phases observed in several systems of transition metal dioxides [1-3]. It has also been pointed out that there exists a close relationship between the metal-metal distances and the number of excess valence electrons available per close metal-metal contact [1,2]. This relation is particularly evident if some kind of normalized metal-metal distance is used, giving a certain allowance for the different sizes of the metal atoms. For the rutile-type phases the axial ratio c/a has been found to provide an appropriate normalized distance [3]. In order to investigate the validity of this observation, some further pseudobinary systems of transition metal dioxides have been studied. The investigations have been concentrated on rutile-type phases. A thorough phase analysis was not aimed at.

The samples investigated comprised mixed dioxides of titanium, niobium, chromium and molybdenum. The starting materials were all of high purity. The samples were generally prepared by heating appropriate mixtures of oxides and metals in sealed, evacuated silica tubes and keeping the temperature at about 1 000°C for two days. Since the solubility of MoO_2 in TiO_2 (rutile) was found to be rather limited in specimens prepared in this way, the samples for the $(Ti,Mo)O_2$ systems were melted in an electric arc furnace and then tempered in evacuated silica capsules for two days at about 1 300°C.

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* I, see Ref.[4]

Table 1. Methods of preparation and results of phase analyses.

System	Starting materials	Composition of sample	Heating temperature	X-Ray evidence	Unit cell dimensions of rutile type phase			Ref.
					a Å	c Å	c/a	
TiO_2-NbO_2	TiO_2 (anatase)	$Ti_{0.75}Nb_{0.25}O_2$	1 000°C	Rutile	4.659	2.986	0.6409	4
	Nb_2O_5, Nb	$Ti_{0.50}Nb_{0.50}O_2$		»	4.719	2.997	0.6351	4
		$Ti_{0.25}Nb_{0.75}O_2$		»	4.778	2.999	0.6277	4
		$Ti_{0.20}Nb_{0.80}O_2$		»	4.789	2.999	0.6265	
		$Ti_{0.10}Nb_{0.90}O_2$		»	4.822	3.000	0.6221	
TiO_2-MoO_2	TiO_2 (anatase)	$Ti_{0.75}Mo_{0.25}O_2$	1 300°C	»	4.643	2.939	0.6330	
	MoO_3, Mo	$Ti_{0.50}Mo_{0.50}O_2$		»	4.716	2.899	0.6147	
NbO_2-CrO_2	Nb_2O_5, Nb	$Nb_{0.71}Cr_{0.29}O_2$	1 000°C	»	4.735	3.008	0.6353	
	Cr_2O_3	$Nb_{0.69}Cr_{0.31}O_2$		»	4.727	3.004	0.6355	
		$Nb_{0.67}Cr_{0.33}O_2$		»	4.718	3.006	0.6371	
		$Nb_{0.60}Cr_{0.40}O_2$		»	4.691	3.019	0.6436	
		$Nb_{0.50}Cr_{0.50}O_2$		»	4.645	3.014	0.6489	
		CrO_2		»	4.423	2.917	0.6595	5
NbO_2-MoO_2	Nb_2O_5, Nb	$Nb_{0.60}Mo_{0.40}O_2$	1 000°C	»	4.856	2.925	0.6023	
	MoO_3, Mo	$Nb_{0.50}Mo_{0.50}O_2$		»	4.858	2.912	0.5994	
		$Nb_{0.33}Mo_{0.67}O_2$		»	4.855	2.883	0.5938	4
		$Nb_{0.25}Mo_{0.75}O_2$		»	4.855	2.863	0.5897	
VO_2-CrO_2	V_2O_3, V_2O_5, Cr_2O_3	$V_{0.85}Cr_{0.15}O_2$	1 000°C	Distorted rutile				

The preparations were studied by means of X-ray powder photographs obtained in a Guinier focusing camera with strictly monochromatized Cu$K\alpha_1$ radiation.

The methods of preparation and the results of the phase analyses are summarized in Table 1. Fig. 1 represents the volume and the c/a parameter of the rutile-type phases *versus* the composition of the samples investigated in this and in a previous study[4]. The distortion of the unit cell is obvious for most systems. Thus while the volumes change almost linearly with composition, the axial ratios are far from constant, decreasing markedly with increasing contents of the metal of higher valency except in the systems containing chromium (*v. infra*). This is also demonstrated in Fig. 2 which gives the c/a-values *versus* n, the number of excess valence electrons per close metal-metal contact. The character of the curves is in general agreement with the previously reported observation that c/a (and in most cases also the metal-metal distance) decreases with increasing n. However, the present data also illustrate the minor influence of the individual character of the various metals on the axial ratio. Thus when comparing systems containing titanium as a common component, the lowering of c/a is increased by the other metal in the order vanadium, niobium, molybdenum at compositions with the same concentration of valence

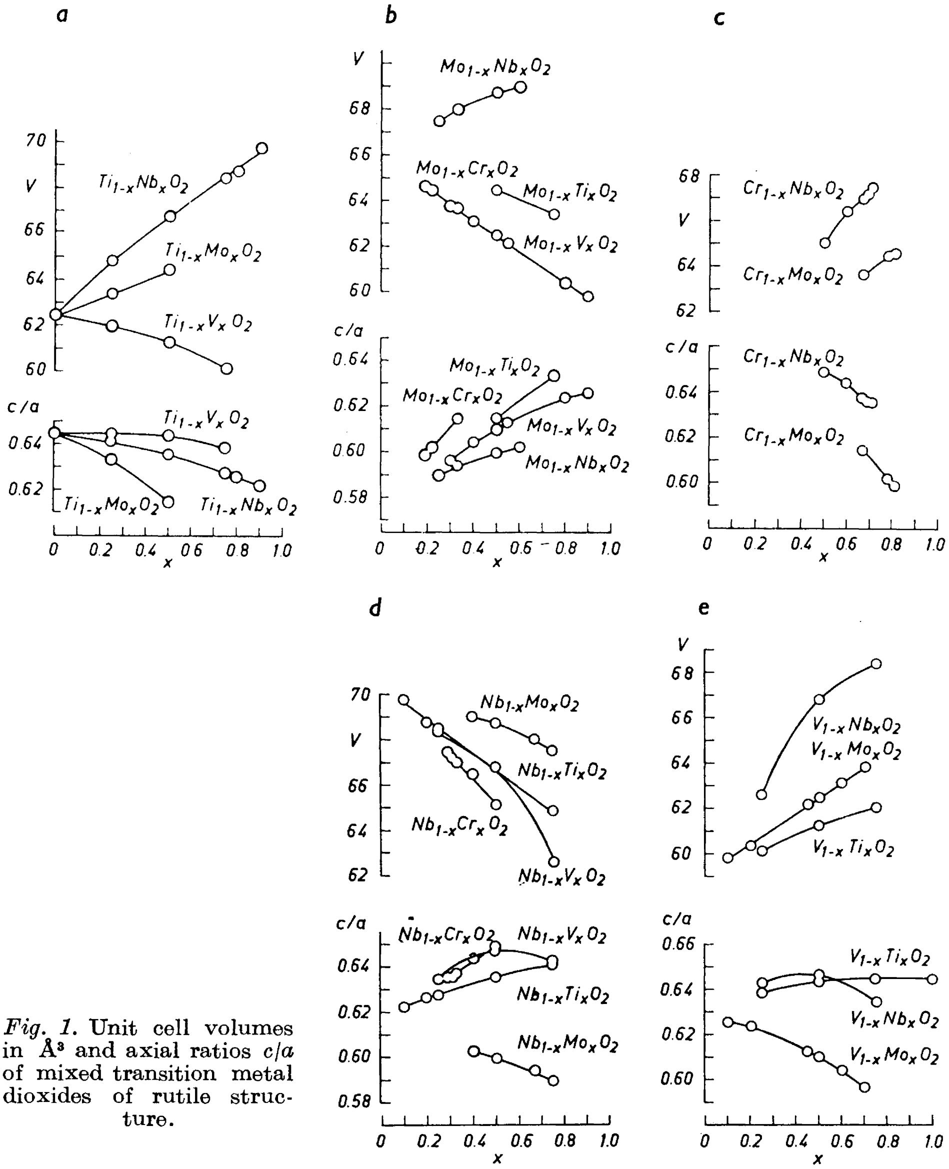

Fig. 1. Unit cell volumes in Å^3 and axial ratios c/a of mixed transition metal dioxides of rutile structure.

electrons (*cf.* Fig. 2). In the systems containing molybdenum the axial ratio is lowered more by niobium than by vanadium, the latter two metals contributing the same number of valence electrons. In this connection the variation of c/a with the composition of the $(V,Nb)O_2$ rutile phase is of interest (*cf.* Figs. 1d and 1e).

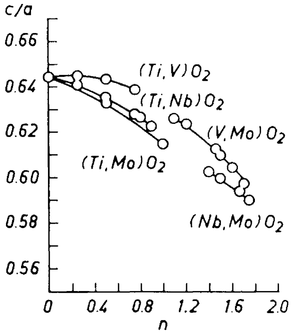

Fig. 2. Axial ratios (c/a) of mixed transition metal dioxides of rutile structure *versus* number of excess valence electrons per close metal-metal contact (n).

The present study confirms the divergent behaviour shown by chromium in rutile-type phases including chromium dioxide [5,6]. Thus the depression of c/a is less for chromium than for titanium and molybdenum in rutile samples containing niobium (Fig. 1d) and less than for titanium, vanadium and niobium in samples with molybdenum as the other component (Fig. 1b). The presence of excess valence electrons contributed by chromium atoms evidently does not cause a reduction of the metal-metal distance or the axial ratio similar to that produced by, for example, the "isoelectronic" molybdenum atoms. The calculation of n values disregarding the chromium electrons is somewhat arbitrary as it involves the assignment of a numerical valency to chromium. On the other hand an estimation of the charge of the chromium atoms from the c/a values of the present rutile phases would be rather uncertain (*cf.* Ref. [6]).

Further studies on these phases including magnetic measurements and X-ray investigations at elevated temperatures are being planned.

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