Rutile-Type Phases in Some Systems of Mixed Transition Metal Dioxides

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It has previously been pointed out that, in some dioxides of transition metals, very short metal-metal distances are present, indicating the existence of bonds between the metal atoms. This is the case for the dioxides of MoO$_2$-type [1] and for orthorhombic rhenium dioxide [2]. In the search for further substances exhibiting such bonds, one pseudo-ternary and several pseudo-binary systems of transition metal dioxides have been studied. Since the intention was principally to find the metal-metal distances, it was natural to concentrate the interest on the occurrence of phases of rutile type, where the intermetallic distances are simply connected with the unit cell dimensions. A comprehensive knowledge of the phase relations in the various systems was not aimed at. This article presents the findings obtained during these studies. Discussions of the occurrence of metal-metal bonds in the various systems have been given elsewhere [3-5].

The samples investigated comprised mixed dioxides of titanium, vanadium, niobium, chromium, molybdenum, wolfram and rhenium. The starting materials were all of high purity. The samples were generally prepared by heating appropriate mixtures of oxides and sometimes also metals in sealed, evacuated silica tubes and keeping the temperature at about 1 000°C for several days. This treatment was with few exceptions found satisfactory for the attainment of equilibrium conditions.

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. Potassium chloride (a = 6.2919 Å at 20°C) [6] was always added to the powder specimens as an internal standard. The results of the phase analysis are summarized in Table 1 which also includes some data reported by Schönberg [7].

A noticeable feature of several of the systems investigated is the occurrence of rutile-type phases (r) existing over wide ranges of composition (*cf.* Fig. 1). This is the case not only in systems containing a component of rutile structure (*i.e.* the systems with titanium dioxide). Systems formed with components of other crystal structures, including vanadium and molybdenum dioxide (MoO$_2$-structure) [1], niobium dioxide (superstructure of distorted rutile) [5] and rhenium dioxide (orthorhombic ReO$_2$-type) [2] also show intermediary regions of ideal rutile type. These results evidently add further examples to the data given by Brandt [8], of the pronounced adaptability of the rutile structure to a variety of metal atom species.

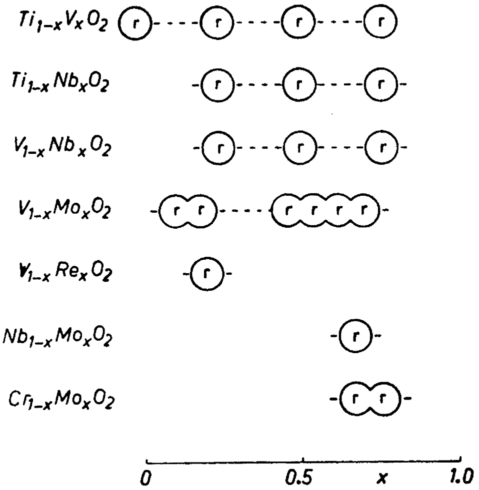

Fig. 1.

In no case were indications observed of superstructures like those reported by Byström, Hök and Mason [9] for the large group of mixed oxides of ordered trirutile type. No attempts were made in this study to find out if such ordering occurs at lower temperatures.

The occurrence at an intermediary composition in the molybdenum dioxide-wolfram dioxide system of a MoO$_2$-type phase (which may extend over the entire range of composition) is evidently rather exceptional. Probably a mixed MoO$_2$-type structure will form over a wide range of composition only if the structures of the two components are similar.

This investigation forms part of a research program on metal oxides and related com-

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

System	Starting materials	Composition of sample	X-Ray evidence	Unit cell dimension of rutile type phase		Ref.
				a Å	*c* Å	
TiO_2-VO_2	TiO_2(anatase), V_2O_5, V or TiO_2(anatase), V_2O_5, V_2O_3	TiO_2	Rutile	4.593	2.959	10
		$Ti_{0.75}V_{0.25}O_2$	Rutile	4.581	2.954	
		$Ti_{0.50}V_{0.50}O_2$	Rutile	4.566	2.938	
		$Ti_{0.25}V_{0.75}O_2$	Rutile	4.550	2.905	
		$Ti_{0.20}V_{0.80}O_2$	Orthorhombic phase			
TiO_2-NbO_2	TiO_2(anatase), Nb_2O_5, Nb	TiO_2	Rutile	4.593	2.959	10
		$Ti_{0.75}Nb_{0.25}O_2$	Rutile	4.659	2.986	
		$Ti_{0.50}Nb_{0.50}O_2$	Rutile	4.719	2.997	
		$Ti_{0.25}Nb_{0.75}O_2$	Rutile	4.778	2.999	
TiO_2-TaO_2			Rutile			7
TiO_2-MoO_2	TiO_2(anatase), MoO_3, Mo		Low solubility of MoO_2 in TiO_2 (rutile)			
TiO_2-ReO_2	TiO_2(anatase), ReO_3, Re		Low solubility of ReO_2 in TiO_2 (rutile)			
VO_2-NbO_2	V_2O_5, V_2O_3, Nb_2O_5, Nb	$V_{0.25}Nb_{0.75}O_2$	Rutile	4.759	3.018	
		$V_{0.50}Nb_{0.50}O_2$	Rutile	4.692	3.033	
		$V_{0.75}Nb_{0.25}O_2$	Rutile	4.602	2.956	
VO_2-TaO_2			Rather low solubility of VO_2 in TaO_2(rutile type)			7
VO_2-MoO_2	V_2O_5, V_2O_3, MoO_3, Mo	$V_{0.90}Mo_{0.10}O_2$	Rutile	4.573	2.860	
		$V_{0.80}Mo_{0.20}O_2$	Rutile	4.591	2.864	
		$V_{0.55}Mo_{0.45}O_2$	Rutile	4.664	2.857	
		$V_{0.50}Mo_{0.50}O_2$	Rutile	4.680	2.854	
		$V_{0.40}Mo_{0.60}O_2$	Rutile	4.709	2.845	
		$V_{0.30}Mo_{0.70}O_2$	Rutile	4.747	2.831	
VO_2-MoO_2-ReO_2	MoO_3, V_2O_3, Re	$V_{0.33}Mo_{0.50}Re_{0.17}O_2$	Rutile	4.742	2.818	
VO_2-ReO_2	V_2O_5, Re	$V_{0.80}Re_{0.20}O_2$	Rutile	4.612	2.835	
NbO_2-MoO_2	MoO_3, Nb	$Nb_{0.33}Mo_{0.67}O_2$	Rutile	4.855	2.883	
CrO_2-MoO_2	Cr_2O_3, MoO_2, MoO_3	$Cr_{0.33}Mo_{0.67}O_2$	Rutile	4.696	2.886	4
		$Cr_{0.22}Mo_{0.78}O_2$	Rutile	4.749	2.858	
MoO_2-WO_2	MoO_3, Mo, WO_3, W	$Mo_{0.50}W_{0.50}O_2$	Deformed rutile (MoO_2-type)			

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The Preparation of Some Naphthylselen-carboxylic Acids

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In connection with the studies on synthetic plant growth regulators going on at this institute some naphthylsulphide-carboxylic acids have previously been prepared [1,2] and the plant growth regulating activity has been investigated by Professor B. Åberg at the Royal Agricultural College, Uppsala [3]. We have now extended these studies to some naphthylselen-carboxylic acids.

Some phenylselenacetic acids and 1-naphthylselenacetic acid have previously been prepared by reacting the Grignard reagents with selenium and then adding dilute alkali solution and bromoacetic acid [4]. As bromobenzene and 1-bromonaphthalene are readily available this method seems to be convenient for the preparation of phenylselen-carboxylic acids and for 1-naphthylselen-carboxylic acids. For the syntheses of the 2-naphthylselen-carboxylic acids we have tried three methods:

Acid	Method	Yield	M.p.
1-Naphthylselen-acetic	2	50	66—67°*
2-Naphthylselen-acetic	1	26	89—90 °
2-Naphthylselen-acetic	2	20	89—90 °
2-Naphthylselen-acetic	3	75	89—90 °
α-(2-Naphthylselen)-propionic	1	20	118—119 °
α-(2-Naphthylselen)-propionic	2	15	118—119 °
α-(2-Naphthylselen)-propionic	3	77	118—119 °
β-(2-Naphthylselen)-propionic	2	14	105—106 °

* Morgan and Porritt reported m.p. 54°.

1. Hydrolysis of 2-naphthylselenocyanate [5] and direct reaction with different bromosubstituted acids.
2. Reaction of selenium with the Grignard reagent of 2-iodonaphthalene and further reaction with halogen substituted acids.
3. Reduction with sodiumborohydride of 2,2'-dinaphthyldiselenide dissolved in a benzene-alcohol mixture followed by reaction with haloesters.

As can be seen in the table above, method 1 has given a somewhat higher yield (counted on 2-naphthylselenocyanate) than method 2 (counted on 2-iodonaphthalene). However, 2-iodonaphthalene is much easier to prepare than 2-naphthylselenocyanate, and so method 2 is to be preferred. Both in method 1 and 2 some diselenide is formed from which the acids can be obtained in very good yield. If the diselenide is accessible, this method is certainly the best.

Experimental. Method 1. 2-Naphthylselenocyanate was prepared according to Loevenich, Fremdling and Föhr [5]. The naphthylselenocyanate was dissolved in hot alcohol, some glucose and excess of concentrated potassium hydroxide solution were added and the mixture boiled until a homogeneous phase had been obtained. The mixture was cooled and the neutralised bromosubstituted acid was added. After standing in a closed bottle for 12 h warm water was added, the mixture filtered and the solution acidified with hydrochloric acid.