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COMPLEX ALKALI TITANIUM OXIDES $A_x(B_yTi_{8-y})O_{16}$ OF THE
 α - MnO_2 STRUCTURE-TYPE

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α - MnO_2 , one of the numerous modifications of manganese dioxide (Glemser *et al.*, 1961; Gattow and Glemser, 1961a,b), exhibits a particularly interesting crystal structure (Byström and Byström, 1950). In this tetragonal structure (MnO_6)-octahedra form a rather open framework with channels in the direction of the c axis. Obviously the structure is stabilized by large alkali or alkaline earth ions in the channels. Isostructural with α - MnO_2 are the manganese minerals cryptomelane, hollandite and coronadite. Complete substitution of manganese by titanium and iron or titanium and chromium has been found in the minerals priderite (Norrish, 1951) and redledgeite (Strunz, 1963), resp. By synthesis potassium-priderite (Norrish, 1951) and compounds of a series $Ba_x(Mg_xTi_{8-x})O_{16}$ (Dryden and Wadsley, 1958) could be prepared. The chemical composition of these various compounds indicates the tolerance of the α - MnO_2 structure to substitutions for A-ions (channels) and B-ions (framework). In addition, the positions of the large A-ions may be occupied incompletely leading to complex non-stoichiometric oxides. It has been reported recently (Bayer and Hoffmann, 1965) that substitution of sodium by potassium or by rubidium in $Na_x(B_yTi_{8-y})O_{16}$ (Na_xTiO_2 -type) results in formation of α - MnO_2 -type compounds. Therefore a systematic study of ionic substitution and non-stoichiometry has been

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started also for this structure type. A striking similarity exists between Na_xTiO_2 -type and $\alpha\text{-MnO}_2$ -type compounds with respect to chemical composition and to the tendency for formation of non-stoichiometric compounds, although the structures are quite different.

The compounds listed in Tables 1 and 2 could be prepared by solid-state reaction (oxides, KNO_3 , Rb_2CO_3 , CsNO_3). All samples were heated

TABLE 1. $\alpha\text{-MnO}_2$ -TYPE COMPOUNDS $\text{K}_x(\text{B}_x\text{Ti}_{8-x})\text{O}_{16}$

B	Formula (nominal composition)	Heat treatment		x-ray	Lattice constants	
		Temp. (°C)	Time (h)		a	c (Å)
Al	$\text{K}_{2.25}(\text{Al}_{2.28}\text{Ti}_{5.72})\text{O}_{16}$	1000	20	α , X		
Al	$\text{K}_2(\text{Al}_2\text{Ti}_6)\text{O}_{16}$	1000	20	α	10.04 ₀	2.94 ₀
Al	$\text{K}_{1.78}(\text{Al}_{1.78}\text{Ti}_{6.22})\text{O}_{16}$	1150	15	α	10.05 ₆	2.94 ₀
Al	$\text{K}_{1.60}(\text{Al}_{1.60}\text{Ti}_{6.40})\text{O}_{16}$	1000	20	α	10.06 ₇	2.93 ₉
Al	$\text{K}_{1.45}(\text{Al}_{1.45}\text{Ti}_{6.55})\text{O}_{16}$	1000	20	α , Y, rutile		
Ti	$\text{K}_2(\text{Ti}_2^{3+}\text{Ti}_6^{4+})\text{O}_{16}$	1000	24	α	10.17 ₀	2.95 ₈
Cr	$\text{K}_2(\text{Cr}_2\text{Ti}_6)\text{O}_{16}$	1100	48	α	10.12 ₅	2.95 ₅
Fe	$\text{K}_2(\text{Fe}_2\text{Ti}_6)\text{O}_{16}$	1100	48	α	10.14 ₃	2.96 ₉
Ga	$\text{K}_2(\text{Ga}_2\text{Ti}_6)\text{O}_{16}$	1100	92	α	10.11 ₉	2.96 ₂

 $\alpha\text{-MnO}_2$ -TYPE COMPOUNDS $\text{K}_x(\text{B}_{x/2}\text{Ti}_{8-x/2})\text{O}_{16}$

B	Formula (nominal composition)	Heat treatment		x-ray	Lattice constants	
		Temp. (°C.)	Time (h)		a	c (Å)
Mg	$\text{K}_2(\text{MgTi}_7)\text{O}_{16}$	1000	20	α	10.15 ₇	2.97 ₄
Co	$\text{K}_2(\text{CoTi}_7)\text{O}_{16}$	1100	92	α	10.13 ₉	2.97 ₅
Ni	$\text{K}_2(\text{NiTi}_7)\text{O}_{16}$	1100	92	α	10.14 ₀	2.96 ₅
Cu	$\text{K}_2(\text{CuTi}_7)\text{O}_{16}$	850	20	α	10.13 ₅	2.97 ₇
Zn	$\text{K}_2(\text{ZnTi}_7)\text{O}_{16}$	1100	92	α	10.16 ₁	2.97 ₃

$\alpha = \alpha\text{-MnO}_2$ -type

in an oxidizing atmosphere (air) except samples containing Ti^{3+} (vacuum). Formulas have been calculated from nominal compositions. This seems to be justified since long exposure x-ray diagrams showed only a single phase for all samples with K and Rb, and because changes in chemical composition due to volatilization are unlikely at the temperatures used in preparation. In the case of K-Al-Ti-oxides an unknown phase occurred in addition to the stoichiometric compound $\text{K}_2(\text{Al}_2\text{Ti}_6)\text{O}_{16}$ when excess potassium was used in the batch composition. Pure non-stoichiometric compounds of the $\alpha\text{-MnO}_2$ -type were found down to about

$K_{1.60}(Al_{1.60}Ti_{6.40})O_{16}$. With lower potassium concentrations rutile and a second, unknown phase showed up in the x -ray diagrams. Lattice constants were determined from Guinier powder patterns using CuK_{α} radiation and Si as internal standard. All x -ray diagrams could be indexed on a tetragonal cell.

Indexed d -spacings of $K_2(MgTi_7)O_{16}$ are compared to those of priderite and cryptomelane in Table 3. Splitting of reflections was never observed, even with the high resolution of the Guinier camera (after Jagodzinski).

TABLE 2. α - MnO_2 -TYPE COMPOUNDS $Rb_x(B_xTi_{8-x})O_{16}$

B	Formula (nominal composition)	Heat treatment		x -ray	Lattice constants	
		Temp. (°C.)	Time (h)		a	c (Å)
Al	$Rb_2(Al_2Ti_6)O_{16}$	1000	20	α	10.10 ₂	2.94 ₁
Ti	$Rb_2(Ti_2^{3+}Ti_6^{4+})O_{16}$	1000	23	α	10.21 ₀	2.96 ₈
Cr	$Rb_2(Cr_2Ti_6)O_{16}$	1000	20	α	10.16 ₈	2.95 ₇
Fe	$Rb_2(Fe_2Ti_6)O_{16}$	1000	20	α	10.18 ₉	2.97 ₆
Ga	$Rb_2(Ga_2Ti_6)O_{16}$	1000	20	α	10.16 ₇	2.96 ₄

 α - MnO_2 -TYPE COMPOUNDS $Rb_x(B_{x/2}Ti_{8-x/2})O_{16}$

B	Formula (nominal composition)	Heat treatment		x -ray	Lattice constants	
		Temp. (°C)	Time (h)		a	c (Å)
Mg	$Rb_2(MgTi_7)O_{16}$	1000	26	α	10.19 ₅	2.97 ₈
Co	$Rb_2(CoTi_7)O_{16}$	1000	26	α	10.20 ₂	2.97 ₈
Ni	$Rb_2(NiTi_7)O_{16}$	1100	28	α	10.19 ₁	2.96 ₇
Cu	$Rb_2(CuTi_7)O_{16}$	1000	26	α	10.19 ₆	2.98 ₀
Zn	$Rb_2(ZnTi_7)O_{16}$	1000	26	α	10.20 ₃	2.97 ₆

Besides tetragonal symmetry, a weak monoclinic deformation of the unit cell is also known for the minerals cryptomelane and hollandite (Byström and Byström, 1950; Mathieson and Wadsley, 1950). This monoclinic deformation has been found so far only in manganese minerals containing several A-ions of different size. Ordered distribution then may cause lowering of symmetry (Gehlen, 1958).

There are the following possibilities for order-disorder transitions in complex oxides of the α - MnO_2 structure-type: distribution of different A-ions, distribution of A-ions in non-stoichiometric compositions, and distribution of B-ions. These transitions have not been investigated so far and therefore it cannot be decided which one affects the symmetry.

Non-stoichiometric compositions $K_x(Al_xTi_{8-x})O_{16}$ are listed in Table 1 as an example. There were no difficulties in preparing stoichiometric

TABLE 3. X-RAY POWDER DATA FOR $K_2(MgTi_7)O_{16}$, PRIDERITE (NORRISH, 1951) AND CRYPTOMELANE (MATHIESON AND WADSLEY, 1950)

$K_2(MgTi_7)O_{16}$			Priderite			Cryptomelane	
d (Å)	I	hkl	d (Å)	I	hkl	d (Å)	I
7.16	m	110	7.14	70	110	6.98	40
5.08	m	200	5.05	70	200	4.97	30
						4.84	50
3.592	w	220	3.58	20	220	3.514	10
						3.454	20
3.211	vs	310	3.20	100	310	3.149	30
						3.110	80
						3.097	30
						3.065	20
			2.85	10	101		
2.538	w	400	2.53	20	400	2.481	30
2.487	s	211	2.47	60	211	2.425	10
2.391	w	330	2.38	10	330	2.399	100
						2.366	5
2.271	w	420	2.26	20	420	2.194	40
2.235	ms	301	2.23	40	301	2.170	30
						2.149	30
2.045	vvw	321	2.04	20	321	2.010	20
1.991	w	510	1.985	20	510	1.907	20
1.896	ms	411	1.891	60	411	1.843	40
						1.820	50
1.794	vw	440	1.701	10	440	1.745	10
1.740	vw	530	1.740	10	530	1.723	10
1.691	m	600	1.687	40	600	1.684	10
1.676	w	501				1.654	80
						1.617	70
1.592	ms	521	1.588	50	521, 620	1.553	10
						1.535	20
1.487	m	002	1.483	40	002		
1.457	vw	112, 611	1.453	20	112, 611		
1.426	vw	202	1.424	10	202		
1.399	m	541	1.397	40	640, 541		
			1.373	10	222		
1.349	w	312	1.347	20	312, 631		
1.333	vw	730	1.330	20	730		
			1.298	10	701		
1.283	vw	402	1.280	20	402		
1.263	vw	332	1.260	20	332, 721		
			1.240	20	422		
1.196	vw	660	1.192	20	660		
TETRAGONAL $a = 10.157 \text{ \AA}$ $c = 2.974 \text{ \AA}$			TETRAGONAL $a = 10.11 \text{ \AA}$ $c = 2.964 \text{ \AA}$			MONOCLINIC $a = 9.79 \text{ \AA}, b = 2.88 \text{ \AA}$ $c^\circ = 9.94 \text{ \AA}, \beta = 90^\circ 37'$	

vs=very strong, s=strong, m=medium, w=weak, vw=very weak

compounds with K and Rb. In the case of Cs only non-stoichiometric phases $Cs_x(B_xTi_{8-x})O_{16}$ with $B = Al, Ti, Cr, Fe, Ga$ and $Cs_x(B_{x/2}Ti_{8-x/2})O_{16}$ with $B = Mg, Co, Ni, Cu, Zn$ could be obtained. All these reaction products gave powder x-ray diffraction patterns showing the α - MnO_2 phase and some additional reflections. The latter can probably be assigned to a Cs-titanate. Therefore it is not possible to specify the composition of the Cs-containing α - MnO_2 phase. The measured tetragonal cell dimensions correspond closely to those of the K- and Rb-compounds with slightly larger lattice constant a .

The A-A-ion distances are already unusually short for the stoichiometric K- and Rb-compounds and correspond to the lattice constant c . In the case of Cs, the diameter of the ion (3.34 Å) is considerably larger than the c axis of the Cs-compounds, therefore a stoichiometric incorporation of Cs into the structure seems to be impossible, even when strong polarization effects are taken into account. This is in accordance with the experimental results.

Byström and Byström (1951) found that only 50% of the Ba-positions are occupied in hollandite crystals which they studied. They assumed a one-dimensionally ordered Ba distribution on the fourfold axis (only every other position is occupied) which is three-dimensionally disordered. Water molecules can be placed on the vacant positions. Our own experiments to prepare stoichiometric Ba-Ti-oxide compounds of the α - MnO_2 structure type, *e.g.*, $Ba_2(Mg_2Ti_6)O_{16}$ were unsuccessful. According to the literature (Dryden and Wadsley, 1958) lower concentrations of barium can be present in the structure channels. Superlattice formation, which is connected undoubtedly with the aforementioned order-disorder transitions, has been found in two cases, for hollandite by Mukherjee (1964) and for redledgeite by Strunz (1963). X-ray patterns of $K_2(Al_2Ti_6)O_{16}$, in which increasing amounts of K were replaced by Ba (up to 60 atomic %), showed superlattice reflections already at low Ba contents (10 atomic %). These could be indexed by doubling the lattice constants a and c .

Compared to the recently described Na_xTiO_2 -type compounds, the α - MnO_2 -type structure shows a greater tolerance for substitution in the octahedral framework. Besides the known compounds of Mn or Ti in combination with Al, Ti^{3+} , Cr, Fe, Ga, Mg, Co, Ni, Cu or Zn, this structure type is possible also for Sb^{5+} in combination with the above tri- and divalent cations. Also Sn^{4+} , combined with correspondingly larger ions, *e.g.*, In^{3+} , can build up the framework of the α - MnO_2 -type structure. Investigations on further substitutions and on order-disorder relations in connection with superlattice formation and lowering of symmetry are presently being carried out.

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INVERTED PHASE RELATION IN THE FORMATION OF NEPHELINE AND CARNEGIEITE FROM THE SYSTEM KAOLINITE—SODIUM CARBONATE

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INTRODUCTION

In the system with the composition NaAlSiO_4 , such phases as low- and high-nepheline with the structure related to that of tridymite and low- and high-carnegieite with the structure related to that of cristobalite