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Identification of Titanium Oxides by X-Ray Powder Patterns

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X-Ray powder data are given for fifteen phases occurring in the titanium-oxygen system.

Recent phase analysis studies carried out at this Institute on the titanium-oxygen system have revealed the existence of several previously unknown titanium oxide phases [1]. The analysis was performed by means of X-ray powder patterns, which were found to provide a powerful tool for the identification of the various oxides, both when occurring pure as well as in mixtures with each other.

The powder patterns were obtained using a Guinier focusing camera (80 mm diameter) with strictly monochromatized Cu$K\alpha_1$ radiation. Reflexions could be registered within the diffraction range $1.25° < \Theta < 43.5°$, the lower limit corresponding to a "cut-off" spacing of 35 Å. Potassium chloride (Analar, British Drug Houses, lattice parameter $a = 6.2919$ Å at 20°C [2]) was added to the powder specimens as an internal standard. The back-ground fogging caused by the fluorescence radiation from titanium was effectively depressed by means of an aluminium foil (35 μ) covering the photographic film. The techniques employed in evaluating the photographs have been described in a previous article [3].

The oxides were prepared from starting materials of high purity, *viz.* titanium metal (99.97 %) and titanium dioxide (99.98 %) by methods described previously [1]. The latter substance was found to be of the anatase form and was consequently used for registering the powder pattern of this modification of the dioxide.

All the synthesized oxides were obtained in a pure state except the so-called δ-phase ($TiO_{\sim 0.65}$) which always appeared together with Ti_2O and TiO (low-temperature form). The tables list parts of the powder patterns suitable for identification purposes, ranging from the lower "cut-off" limit

Table 1. α-Ti and Ti_2O. The hexogonally close-packed structure of α-Ti can dissolve considerable amounts of oxygen in a random distribution. At an oxygen content of about $TiO_{0.3}$, a transition occurs to an ordered arrangement of the oxygen atoms. The maximum solubility of oxygen corresponds to the composition Ti_2O, the powder pattern of which is given below. Reflexions indicating the ordered state are indicated by asterisks. The unit cell dimensions for Ti_2O are $a = 2.959_3$ Å and $c = 4.845_4$ Å.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
vvw	0.02536	001*	0.02527
m	0.09028	100	0.09033
m	0.10108	002	0.10108
v st	0.11568	101	0.11560
st	0.19135	102	0.19141
vw	0.22740	003*	0.22743
st	0.27092	110	0.27099
m	0.31785	103	0.31776
vw	0.36141	200	0.36132
m	0.37215	112	0.37207
m	0.38666	201	0.38659
w	0.40429	004	0.40432
w	0.46240	202	0.46240

Table 2. δ-Titanium oxide ($TiO_{\sim 0.65}$).

I	$\sin^2\Theta_{obs}$
st	0.09526
st	0.10332
w	0.16678
m	0.19858
m	0.28590
w	0.29385
w	0.38136

Table 3. TiO (low-temperature form)

I	$\sin^2\Theta_{obs}$
w	0.01906
w	0.02997
w	0.03466
m	0.04206
st	0.05392
m	0.06826
m	0.07613
m	0.07723
w	0.09946
st	0.10183
st	0.10377
st	0.13475
v st	0.13862
vw	0.15741
vw	0.16814
vw	0.19160
w	0.20472
vw	0.20835
w	0.21542
w	0.22115
w	0.22590

Table 4. TiO (NaCl-type). At temperatures above 1 000°C this phase has a very wide homogeneity range which, however, decreases considerably at lower temperatures. At 800°C the phase only exists at a composition very close to $TiO_{1.20}$. The pattern given below corresponds to the sample $TiO_{1.00}$, the cube edge of which is $a = 4.182_2$ Å.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
st	0.10172	111	0.10176
v st	0.13578	200	0.13568
v st	0.27137	220	0.27136
m	0.37305	311	0.37312
m	0.40704	222	0.40704

Table 5. Ti_2O_3. The phase has a very narrow range of homogeneity. The actual sample was of the composition $TiO_{1.500}$ with the lattice parameters of the hexagonal structure, $a = 5.155$ Å, $c = 13.607$ Å.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
m	0.04262	102	0.04258
m	0.08095	014	0.08104
m	0.08929	110	0.08929
w	0.11808	113	0.11813
vvw	0.13202	202	0.13187
w	0.17035	204	0.17032
v st	0.20452	116	0.20465
vw	0.22116	212	0.22116
w	0.25966	214	0.25961
m	0.26787	300	0.26787

Table 6. Ti_3O_5. Dimensions of the monoclinic unit cell: $a = 9.757$ Å, $b = 3.802$ Å, $c = 9.452$ Å and $\beta = 93.11°$.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
vw	0.00669	001	0.00666
vvw	0.02662	002	0.02664
m	0.03239	201	0.03236
v st	0.04736	110	0.04729
vw	0.05025	$20\bar{2}$	0.05024
w	0.05302	202	0.05304
w	0.05359	$11\bar{1}$	0.05360
w	0.05426	111	0.05430
m	0.05995	003	0.05995
vw	0.07323	$11\bar{2}$	0.07323
m	0.08284	$20\bar{3}$	0.08284
w	0.08706	203	0.08704
w	0.10497	311	0.10500
w	0.10615	$11\bar{3}$	0.10618
w	0.10793	401	0.10806
st	0.12375	$40\bar{2}$	0.12384
st	0.13429	204	0.13436
st	0.16415	020	0.16415
m	0.20796	314	0.20805

Table 7. Ti_4O_7

I	$\sin^2\Theta_{obs}$
vw	0.01559
w	0.02143
st	0.03248
w	0.04166
v st	0.05192
w	0.05288
w	0.06135
v st	0.06504
m	0.07011
v st	0.07481
st	0.07560
st	0.08576
vw	0.09210
st	0.09316
st	0.09671
st	0.10109
w	0.10748

Table 8. Ti_5O_9. Dimensions of the triclinic unit cell: $a = 5.569$ Å, $b = 7.120$ Å, $c = 8.865$ Å, $\alpha = 97.55°$, $\beta = 112.34°$, $\gamma = 108.50°$

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
vw	0.00973	001	0.00962
w	0.02194	$10\bar{1}$	0.02189
vw	0.02665	100	0.02664
st	0.03643	$10\bar{2}$	0.03638
vw	0.05063	101	0.05061
v st	0.05226	$1\bar{2}0$	0.05224
vw	0.05294	$02\bar{1}$	0.05294
w	0.05676	020	0.05674
w	0.06091	$\bar{1}21$	0.06091
v st	0.06278	$1\bar{2}1$	0.06279
w	0.06841	$02\bar{2}$	0.06837
v st	0.07010	$10\bar{3}$	0.07011
m	0.07986	021	0.07978
st	0.08737	$20\bar{1}$	0.08744
vw	0.08886	$\bar{1}22$	0.08882
st	0.09384	102	0.09382
st	0.09633	$12\bar{1}$	0.09635
vw	0.10081	$2\bar{2}0$	0.10100
m	0.10297	$02\bar{3}$	0.10303
w	0.10654	200	0.10654
w	0.10867	$\bar{2}22$	0.10877

Table 9. Ti_6O_{11}

I	$\sin^2\Theta_{obs}$
w	0.02410
st	0.03915
v st	0.05224
w	0.05638
st	0.06115
v st	0.06722
w	0.07372
m	0.08212
vw	0.08601
st	0.08841
st	0.09399
st	0.09586
st	0.10421
vw	0.10903

Table 10. Ti_7O_{13}

I	$\sin^2\Theta_{obs}$
w	0.02676
vw	0.03932
st	0.04144
v st	0.05260
w	0.05432
st	0.06028
vw	0.06121
v st	0.06545
w	0.06734
vw	0.07844
vw	0.08233
m	0.08415
w	0.08598
m	0.08955
st	0.09432
st	0.09597
w	0.10264
w	0.10539
w	0.10961

Table 11. Ti_8O_{15}

I	$\sin^2\Theta_{obs}$
w	0.02915
st	0.04311
v st	0.05288
st	0.05966
v st	0.06409
m	0.08548
st	0.09037
st	0.09450
st	0.09590
w	0.10147
w	0.10623

Table 12. Ti_9O_{17}

I	$\sin^2\Theta_{obs}$
vw	0.02380
vw	0.03139
st	0.04453
w	0.05277
st	0.05310
w	0.05777
st	0.05927
st	0.06311
vw	0.06414
st	0.08661
st	0.09091
st	0.09464
st	0.09590
w	0.10071
m	0.10736
m	0.10903

Table 13. $Ti_{10}O_{19}$

I	$\sin^2\Theta_{obs}$
vw	0.03295
v st	0.04516
w	0.05155
v st	0.05271
v st	0.05959
v st	0.06308
vw	0.06890
vw	0.07223
vw	0.08370
st	0.08646
st	0.09019
st	0.09479
st	0.09616
m	0.10238
m	0.10670
m	0.10968

Table 14. TiO_2 *(rutile).* Narrow range of homogeneity. The pattern refers to a sample of stoichiometric composition. Dimensions of the tetragonal unit cell: a = 4.593 Å, c = 2.959 Å.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
st	0.05623	110	0.05626
m	0.09589	101	0.09588
vw	0.11260	200	0.11252
w	0.12399	111	0.12401
w	0.14070	210	0.14065
st	0.20835	211	0.20840
m	0.22501	220	0.22504
w	0.27114	002	0.27102
w	0.28122	310	0.28130
w	0.32093	301	0.32092
vw	0.32716	112	0.32728

Table 15. TiO_2 (anatase). Dimensions of the tetragonal unit cell: $a = 3.786$ Å, $c = 9.517$ Å.

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
v st	0.04798	101	0.04795
vw	0.10030	103	0.10035
st	0.10482	004	0.10480
vw	0.10891	112	0.10900
st	0.16558	200	0.16560
m	0.20522	105	0.20515
m	0.21347	211	0.21355
vw	0.26599	213	0.26600
m	0.27043	204	0.27040
vw	0.31878	116	0.31860
vw	0.33116	220	0.33120
m	0.37075	215	0.37075

and upwards. The phases are of stoichiometric composition if not otherwise stated in the tables.

The effectiveness of the powder patterns for the identification of the titanium oxides may be illustrated by the following example, encountered when analyzing the composition region around the phase Ti_6O_{11}. Photographs of samples TiO_x differing in composition from that of the pure phase by $\Delta x = \pm 0.002$ clearly showed weak extra reflexions which were identified as the strongest lines of the neighbouring phases ($\sin^2\Theta = 0.07011$ of Ti_5O_9 and $\sin^2\Theta = 0.06545$ of Ti_7O_{13}, respectively). The approximate amounts of the extra phases were thus about 5 % of the sample. The exposure times used for these photographs were of normal length, *viz.* one hour. Since the background of the films was quite low, considerably longer exposure times might have been applied, which would correspondingly increase the sensitivity of the method for the identification of minute amounts of extra phases.

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REFERENCES

1. Andersson, S., Collén, B., Kuylenstierna, U. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1641.
2. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
3. Westman, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1587.

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