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A crystallographic study of $Nb_2O_5.3WO_3$.

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The existence of the compound $Nb_2O_5.3WO_3$ was first noted by Goldschmidt (1960). More recently Kovba & Trunov (1962), from a powder diffraction study, have indicated its probable unit cell as tetragonal with $a = 12{\cdot}166 \pm 0{\cdot}003$ kX and $c = 3{\cdot}9265 \pm 0{\cdot}004$ kX. As part of a study of the equilibria in the system Nb_2O_5–WO_3 it was possible, in the present investigation, to grow and isolate single crystals of this compound sufficiently large to permit a diffraction study. This note reports the results of this investigation.

The compound was formed by annealing pressed briquettes of Nb_2O_5 and WO_3 powders, mixed in appropriate proportions, at 1200 °C for one week. Microscopic examination of the fired and air quenched samples revealed translucent needle shaped crystals most of which were very small or twinned. However, a few of the larger crystals with approximate dimensions of $6 \times 20\ \mu$ which appeared free of any visual imperfections could be isolated and properly mounted for the X-ray investigation.

Diffraction studies of the single crystals in a precession camera confirmed the unit cell as tetragonal. The unit-cell dimensions derived from the precession photographs are as follows:

$$a = 12{\cdot}130 \pm 0{\cdot}002,\ c = 3{\cdot}936 \pm 0{\cdot}002\ \text{Å}.$$

Using loose powder samples of the compound, an approximate pycnometric density of 5·3 g.cm^{-3} corresponding to two formula weights per cell (calculated density: 5·51 g.cm^{-3}) was obtained. From the single-crystal photographs, the Laue symmetry of the compound is 4/*mmm*. The only systematic absences appeared to be the odd *h*00 reflections suggesting the presence of a 2_1 screw axis. However, the observable *h*00 reflections in the single-crystal photographs are very weak, and furthermore, since the powder pattern of the compound showed unmistakably the presence of the 300 reflection, the possible space group is $P\bar{4}m2$, *P*4*mm*, *P*42 or *P*4/*mmm*.

The *hk*0 layer photographs of $Nb_2O_5.3WO_3$ in addition to the main reflections, also revealed three additional symmetry unrelated reflections at $\sin\theta/\lambda = 0{\cdot}138$, 0·146 and 0·157 Å^{-1}. These reflections are very weak, and they are so located that the *a* parameter is exactly doubled if they are taken into account.

It appears that these are probably the superstructure type reflections, the occurrence of which has been often discussed in connection with compounds, structurally very closely related to $Nb_2O_5.3WO_3$. For example, Kovba & Trunov (1962) in their diffraction studies of several niobate and tantalate compounds have reported such reflections. Similarly, in the investigation of sodium tungsten bronze, occurrence of faint superstructure reflections was noted, although none could be detected for potassium tungsten bronze (Magnéli, 1949). In the present study, the reproducibility of the extra reflections from one sample to the other was very poor indicating that their origin is probably related to the stoichiometry of the compound. Furthermore, attempts to detect any low angle counterpart of these reflections even in photographs exposed as long as over one week were not successful. These three reflections, therefore, have been taken as not to be related to the primary structure of the compound, and in deriving the unit cell dimensions and the space groups they have been ignored.

The *d* spacings and the relative intensity values derived from a powder pattern of the compound are listed in Table 1. Except for certain reflections which were not reported by Kovba & Truno (1962), their results are in general agreement with those reported here.

Table 1. *Powder pattern data*

hkl	d_c	d_o	Relative intensity
110	8·578 Å	8·74 Å	6
200	6·065	6·06	2
210	5·425	5·418	10
220	4·289	4·287	5
300	4·043	4·055	1
001	3·936	3·923	100
310	3·836	3·839	80
101	3·744	3·720	3
111	3·577	3·559	2
320	3·364	3·361	40
201	3·302	3·270	2
211	3·186	3·173	15
400	3·033	3·030	7
410	2·942	2·938	50
221	2·900	2·892	1
330	2·859	2·855	12
311	2·747	2·736	22
420	2·712	2·712	20
321	2·557	2·551	30
401	2·403	2·396	3
510	2·380		
411	2·358	2·347	35
331	2·314	2·307	10
421	2·234	2·230	15
530	2·081	2·083	4
501, 431	2·067	2·058	4
511	2·037	2·034	1
002	1·968	1·945	15
521	1·956		

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References

GOLDSCHMIDT, H. J. (1960). *Metallurgia*, **62**, 373.
KOVBA, L. M. & TRUNOV, V. K. (1962). *Dokl. Akad. Nauk SSSR.* **147**, 622.
MAGNÉLI, A. (1949). *Ark. Kem.* **1**, 213.

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