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X-RAY POWDER DIFFRACTION STUDY OF SOME MINERAL COMPONENTS OF NIOBIUM-TANTALUM FAMILY

S. PRAMATUS and R. KRITAYAKIRANA

Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 5, Thailand

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Summary

Mineral components of niobium-tantalum family from some mines in Thailand have been studied using the X-ray powder diffraction method. Among these are found columbite-tantalite, niobian rutile, and ilmenorutile, mostly mixed with cassiterite. The unit cell dimensions of these minerals are refined by the least-squares method. The powder diffraction data from the powder photographs taken by the Guinier-Hägg focusing camera, are obtained in the form of tables. These photographs can be more quickly and accurately used as local identification standards.

Introduction

Minerals in Thailand are one of the important natural resources and play an important role in the economy of the country. In many mines, especially tin mines, there are mineral components of the niobium-tantalum family mixed in. These mineral components are important in many aspects[1], for example, niobium can be used in the steel manufacturing industry and for encapsulating fuel elements in nuclear reactors. Some metallic niobium compounds of the general formula Nb_3X (X among other elements = Sn, Al, Ge) are superconducting upto unusually high temperatures (max. $\sim 21^\circ K$) which makes them of practical importance. Tantalum is used mainly in pure form, and is valuable because of its good corrosion properties. It is used as an acid-stable material in chemical industry, in surgery for permament reconstructions (not attacked by body fluids and compatible with the tissues), and in electron tube parts.

TABLE 1: POWDER DIFFRACTION DATA OF A NIOBIUM-TANTALUM SAMPLE CONSISTING OF COLUMBITE-TANTALITE AND THREE LINES OF CASSITERITE, COMPARED WITH THE JCPDS POWDER DATA

Columbite-tantalite (Fe, Mn) (Nb, Ta)$_2$O$_6$ Orthorhombic system							Card no. 16–337		
I/I_1	$S-S_o$mm	d_o Å	$\sin^2 \theta_o$	$\sin^2 \theta_c$	d_c Å	*hkl*	d	I/I_1	*hkl*
11	21.40	7.220	.01138	.01140	7.216	020	7.13	12	020
<5	28.89	5.356	.02068	.02069	5.355	110	5.30	4	110
54	42.04	3.695	.04347[c]	.04348	3.694	130	3.66	50	130, 111
				.04358	3.690	111			
<5	43.02	3.612	.04548	.04558	3.608	040	3.57	10	040
10	46.48[a]	3.347	.05296			(110)			
100	52.12	2.992	.06628	.06638	2.990	131	2.96	100	131
				.07122	2.886	050			
10	54.12	2.884	.07134[c]	.07138	2.883	200	2.86	10	200
<5	59.21[a]	2.642	.08498			(101)			
15	61.51	2.547	.09150	.09158	2.545	002	2.53	6	002
				.09412	2.511	051			
18	62.45	2.509	.09423[c]	.09427	2.509	201	2.49	12	201
14	65.25	2.405	.10256	.10256	2.405	060	2.38	12	060
<5	66.25	2.370	.10561	.10567	2.370	221	2.279	2	151
<5	69.94	2.250	.11721	.11722	2.250	032	2.236	4	032
6	70.78	2.224	.11992	.11991	2.225	231	2.207	4	231
7	75.32	2.096	.13504	.13506	2.096	132	2.084	6	132
				.13959	2.062	070			
7	76.70	2.060	.13979[c]	.13985	2.060	241	2.043	4	241
<5	83.19	1.908	.16302	.16295	1.908	202	1.898	6	202
<5	86.10	1.847	.17390	.17393	1.847	260	1.831	10	260
				.18033	1.814	171			
<5	87.83	1.813	.18051[c]	.18064	1.812	152	1.796	4	152, 171
5	89.35	1.784	.18638	.18634	1.784	311	1.772	14	330
<5	90.44[a]	1.764	.19064			(211)			
21	91.33	1.748	.19415	.19414	1.748	062	1.735	12	062
11	92.01	1.736	.19684	.19683	1.736	261	1.721	20	261
13	104.69	1.542	.24952	.24953	1.542	133	1.672	2	331
5	108.39	1.494	.26569	.26551	1.495	262	1.608	2	–
10	109.71	1.478	.27153	.27149	1.478	191	1.534	8	133
17	111.07	1.462	.27760[c]	.27743	1.462	203	1.516	2	190
				.27781	1.461	332			
<5	117.88	1.387	.30856[c]	.30840	1.387	401	1.484	4	262
				.30861	1.387	063			
<5	120.78[b]	1.357	.32203[c]	.32233	1.357	092	1.465	14	203
<5	124.65	1.321	.34023	.34018	1.321	192	1.454	12	191, 332
<5	130.11	1.273	.36630[c]	.36631	1.273	004	1.432	2	400
				.36665	1.272	303			
<5	132.91	1.250	.37983[c]	.37962	1.250	451	1.393	2	–
				.37993	1.250	412			
9	135.38	1.231	.39185[c]	.39177	1.231	372	1.380	2	401
				.39195	1.230	034			
<5	139.27	1.202	.41090	.41095	1.202	461			
16	148.11	1.142	.45465	.45465	1.142	193			
				.46837	1.126	3, 10, 1			
7	150.94	1.125	.46875	.46887	1.125	064			
				.46899	1.125	501			

[a] SnO$_2$ line [b] superimposed with Si line [c] not used in the refinements

As these important and expensive minerals are always found in tailing from tin mines[2], it is interesting to study these mineral components using the X-ray crystallographic method.

Fifteen samples of these mineral components are obtained from the Department of mineral Resources, Ministry of Industry, and the Department of Geology, Chulalongkorn University. They came from mines in Phuket, Phangnga, Ranong, Uthai Thani and Chiang Mai.

The X-ray powder diffraction method is used to identify these minerals. The powder diffraction data were compared with powder diffraction file compiled by JCPDS[3,4] (Joint Committee on Powder Diffraction Standards). The unit cell dimensions are refined by the least-squares method. The powder diffraction data together with the powder photographs can be locally used as identification standards by directly comparing with the powder patterns provided that the same camera is used.

Experimental procedure

These fifteen samples of the mineral components were recrystallized by heating in a furnace. Two methods were used and they gave similar results. In the first method the sample was crushed into powder and heated at 1000°C for two hours. In the second method tiny pieces of the sample and some powder were placed in evacuated and sealed silica tubes and heated at 800°C for twenty four hours.

Powder diffraction patterns were recorded in a Guinier-Hägg-type focussing powder camera (Philips XDC–700)[5] with CuKα_1 radiation ($\lambda = 1.5405981$ Å) using silicon 99.9% ($a = 5.431065$ Å)[6] as internal calibration standard. The powder photographs were taken at 28°C for approximately one to two hours. The positions of diffraction lines on the photographs were measured with a home-made apparatus built from a photographic enlarger. It has a magnification of 10 times (0.01 mm. from 0.1 mm.). Preliminary computation* of powder film data was done by using the program CSPHGUNE[7]. Peak intensities of diffraction lines were measured with a Nonius microdensitometer Model I.

Mineral identification was made by comparing the powder film data with those from the JCPDS powder diffraction file. It was found that all samples consist of more than two minerals. The unit cell dimensions of the component minerals were refined by the least squares method using the program CSPHCENE[7].

Results

By analyzing the powder diffraction data of all samples, the following minerals were found:—

Columbite-Tantalite. Many of the samples were found to be columbite-tantalite with the chemical formula (Fe, Mn) $(Nb, Ta)_2O_6$ mixed with a little cassiterite (SnO_2),

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* The calculations were carried out on IBM 370/ 138 computer at the Computer Service Centre, Chulalongkorn University, using programs described in Ref. 7.

as only three lines of cassiterite were seen in Fig. 1. There were 33 reflections from the columbite-tantalite (Table 1). By comparing with the diffraction lines from the JCPDS powder diffraction file card number 16–337,[8] as shown in the last three columns in Table 1, the two sets of data were found to match satisfactorily. The remaining three lines in the powder pattern were identified as three strongest lines of cassiterite with the interplanar spacings of 3.347, 2.642 and 1.764 Å respectively. The cassiterite diffraction data was shown in Table 11.

TABLE 2: COMPARISON OF THE THREE STRONGEST LINES FROM THIS STUDY WITH THE JCPDS POWDER DATA

d_oÅ			I/I_1			
2.96	3.66	1.721	100	50	20	16–337
2.992	3.695	1.736	100	54	11	This study

Data from the JCPDS powder diffraction file of columbite-tantalite obtained by Nickel *et al.* using Debye-Scherrer camera with a diameter 114.6 centimeters and using diffractometer to record the intensity are compared with data from this experiment. It is found that the values of d-spacings differ by at most 0.04 Å and these are the spacings of the three most intense lines. Table 2 shows this comparison.

The results of the refinement using 21 lines from the powder photograph showed that the columbite-tantalite is orthorhrombic crystal. The unit cell dimensions differed slightly from those reported by Nickel, Rowland and McAdam[8] as shown in Table 3.

TABLE 3: THE UNIT CELL DIMENSIONS OF COLUMBITE-TANTALITE.

Cell parameters Å This experiment		Cell parameters Å Nickel *et al.*
a	5.7665(7)	5.73
b	14.432(2)	14.24
c	5.0909(7)	5.08

Niobian-Rutile. One of the samples was found to consist of three minerals, namely niobian-rutile[9] [Fe_x^{2+} $(Nb, Ta)_{2x}$ $Ti_{1-x}O_2$] with 13 diffraction lines, pyrophanite[10] ($MnTiO_3$) with 8 diffraction lines and metapyrophanite[11] ($MnO.TiO_2$) with one diffraction line. The powder diffraction patterns of these minerals are presented in Fig. 2.

In Table 4, columns 1–4 show the powder diffraction film data from the sample mentioned above. Columns 5–7 and columns 8–10 show the powder data of niobian-rutile and pyrophanite obtained from the refinement respectively. The results were found to agree satisfactorily. The only reflection 110 with the interplanar spacing $d_o = 2.577$ Å belongs to the metapyrophanite ($MnO.TiO_2$). This line does not exist in pyrophanite. Comparison of the pyrophanite and metapyrophanite

TABLE 4: POWDER DIFFRACTION DATA OF A NIOBIUM-TANTALUM SAMPLE CONSISTING OF NIOBIAN-RUTILE AND PYROPHANITE

Niobium-tantalum sample				Niobian-rutile Tetragonal system			Pyrophanite Hexagonal system		
I/I_1	$S-S_o$mm	d_oÅ	$\sin^2\theta_o$	$\sin^2\theta_c$	d_c	*hkl*	$\sin^2\theta_c$	d_c	*hkl*
<5	41.50	3.744	.04234				.04245	3.739	012
100	47.97	3.246	.05630	.05628	3.247	110			
<5	56.80	2.752	.07833				.07827	2.753	104
<5	60.79[a]	2.577	.08937						(110)
<5	61.50	2.548	.09141				.09153	2.546	110
47	63.07	2.486	.09598	.09594	2.487	101			
5	68.54	2.295	.11267	.11256	2.296	200			
44	72.05	2.188	.12399	.12408	2.187	111			
12	77.05	2.052	.14091	.14070	2.054	210			
<5	85.00	1.870	.16964				.16980	1.869	024
<5	92.57	1.727	.19894				.19900	1.727	116
53	94.95	1.687	.20852	.20850	1.687	211			
41	98.96	1.624	.22502	.22513	1.623	220			
<5	107.48	1.506	.26151				.26133	1.507	214
8	109.69	1.479	.27127	.27120	1.479	002			
<5	110.45	1.470	.27465				.27459	1.470	300
<5	111.97	1.452	.28145	.28141	1.452	310			
12	120.63[b]	1.359	.32112	.32107	1.359	301	.32104	1.360	216
6	121.99	1.346	.32748	.32748	1.346	112			
8	143.85	1.170	.43324	.43363	1.170	321			
<5	156.49	1.094	.49616	.49633	1.093	222			

[a] MnO. TiO_2 line

[b] overlapped by Si

TABLE 5: POWDER DIFFRACTION DATA OF TWO TYPES OF PYROPHANITE FROM THE JCPDS POWDER DIFFRACTION FILE.

Metapyrophanite card no. 2–846 Manganese meta titanate $MnTiO_3$ or $MnO.TiO_2$			Pyrophanite card no. 12–435 Manganese titanium oxide $MnTiO_3$		
d Å	I/I_1	*hkl*	d Å	I/I_1	*hkl*
3.76	30	012	3.74	10	012
2.79	100	104	2.76	100	104
2.58	90	110	2.55	70	110
2.25	50	113	2.25	40	113
2.18	––	201	1.88	60	024
1.89	70	204	1.74	70	116
1.749	80	205, 116	1.66	5	018
1.658	10	108	1.52	50	214
1.521	70	214	1.48	50	300
1.483	60	300	1.36	5	1, 0, 10
1.391	––	208	1.35	10	119
1.360	40	1, 0, 10	1.28	5	220
1.283	20	220	1.20	5	
1.202	10	307	1.130	10	
1.131	10	315, 226	1.089	20	
1.088	20	309, 227	1.063	5	
1.060	10	404, 317	1.016	10	
1.012	10	1, 1, 13, 322	0.982	10	
0.972	10	410			

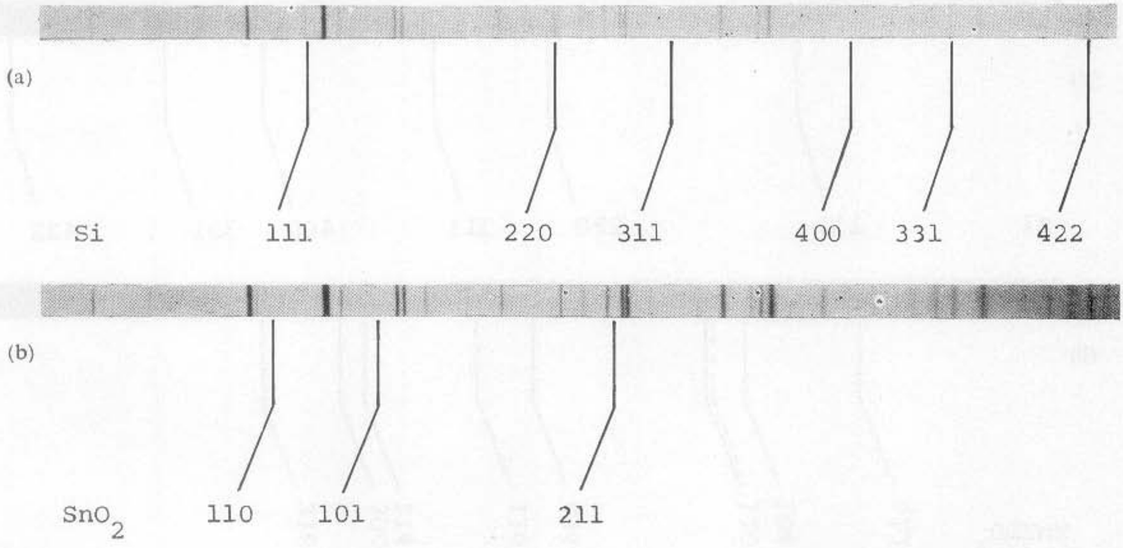

Fig. 1. X-ray powder photographs of columbite-tantalite
(a) mixed with Si, the lines as shown by Miller indices
(b) without Si, the three very weak lines indicated bv Miller indices are those of SnO_2

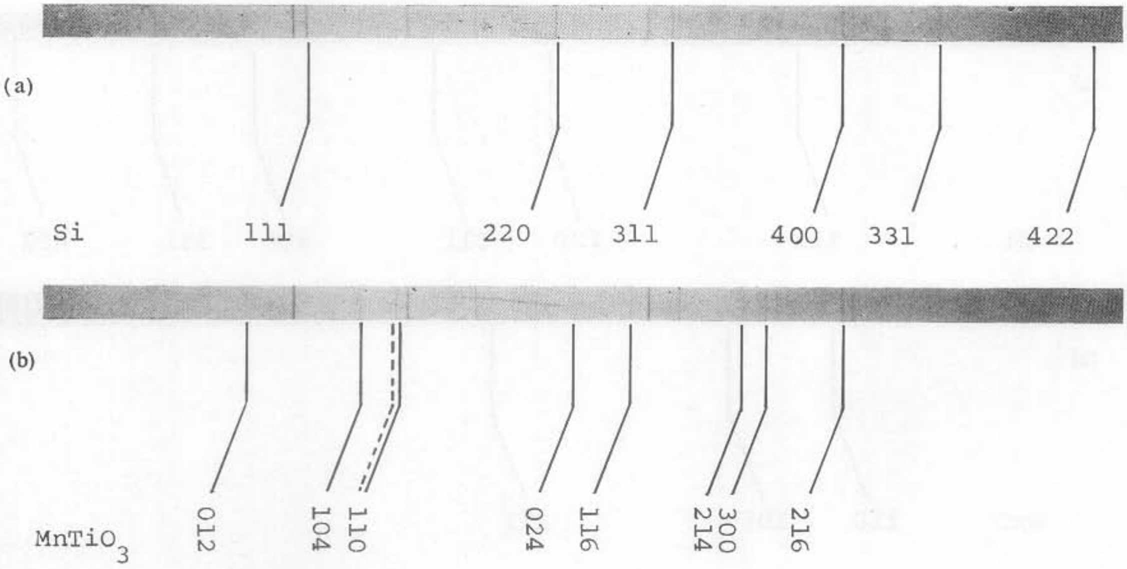

Fig. 2. X-ray powder photographs of a mineral sample consisting of niobian-rutile and pyrophanite

(a) mixed with Si, the lines as shown by Miller indices

(b) without Si, the pyrophanite powder pattern indicated by Miller indices, and one line of metapyrophanite indicated by a dotted line closed to 110 reflection of pyrophanite

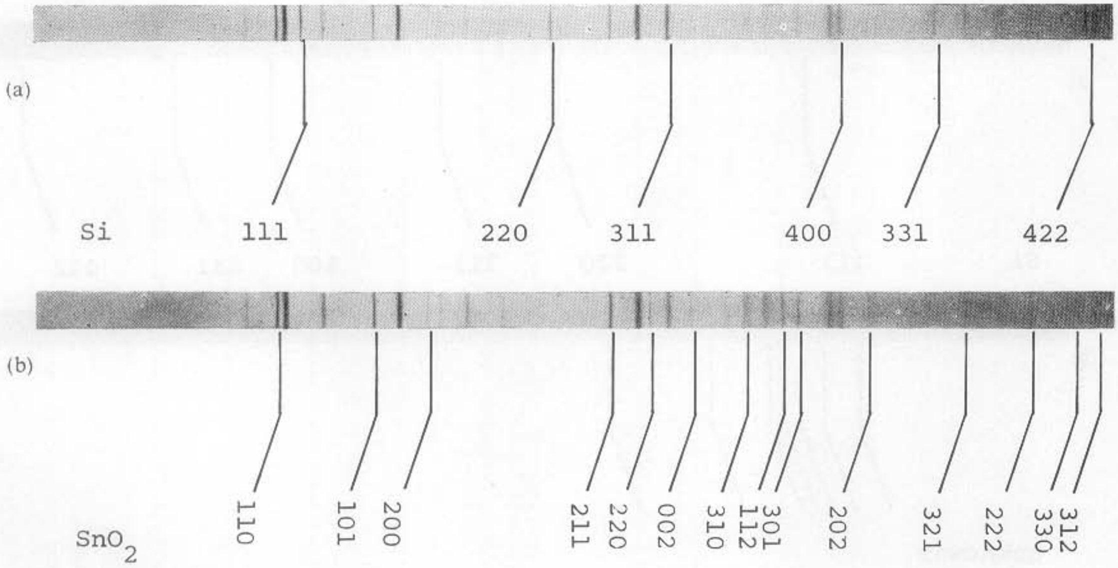

Fig. 3. X-ray powder photographs of ilmenorutile mixed with cassiterite
(a) Si added, the Si-lines indicated by Miller indices
(b) without Si, the cassiterite powder pattern shown by Miller indices

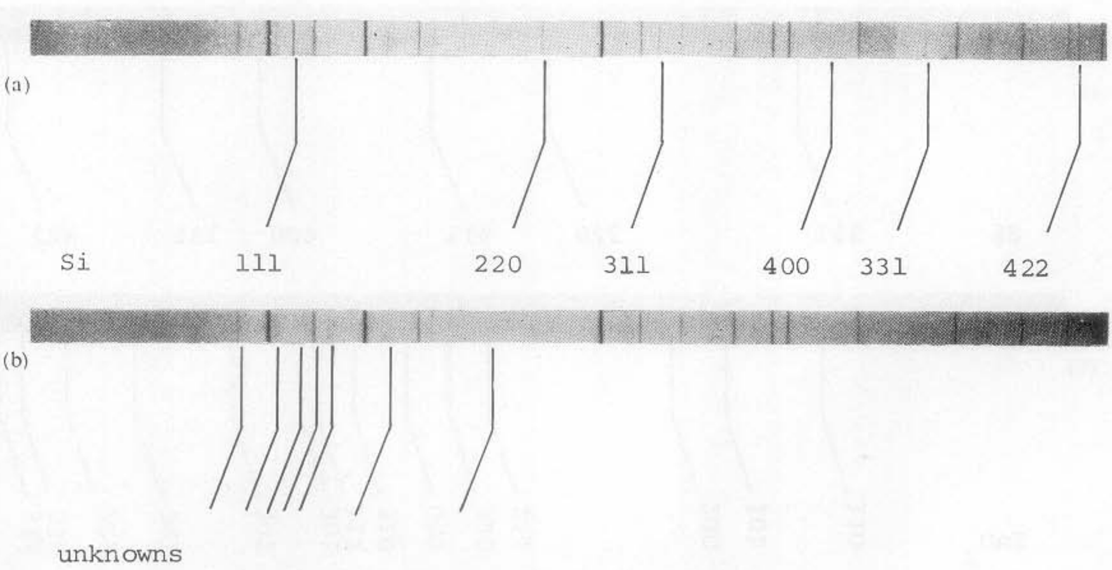

Fig. 4. X-ray powder photographs of cassiterite and some unknowns

(a) Si added, the Si-lines indicated by Miller indices
(b) without Si, showing 7 lines of unknown

TABLE 6: JCPDS POWDER DIFFRACTION DATA OF NIOBIAN-RUTILE AND PYROPHANITE.

Niobian-rutile card no. 11–396 Fe$_x^{2+}$ (Nb, Ta)$_{2x}$Ti$_{1-x}$O$_2$			Pyrophanite card no. 12–435 MnTiO$_3$		
d Å	I/I$_1$	*hkl*	d Å	I/I$_1$	*hkl*
3.23	100	110	3.74	10	012
2.95	<10	001[a]	2.76	100	104
2.48	80	101	2.55	70	110
2.295	10	200	2.25	40	113
2.190	40	111	1.88	60	024
2.051	10	210	1.74	70	116
1.687	90	211	1.66	5	018
1.627	10	220	1.52	50	214
1.481	<10	002	1.48	50	300
1.454	<10	310	1.36	5	1, 0, 10
1.423	<10	102[a]	1.35	10	119
1.361	20	301	1.28	5	220
1.348	<10	112	1.20	5	
1.313	<10	311	1.130	10	
1.247	<10	202	1.089	20	
1.214	<10	212	1.063	5	
1.173	<10	321	1.016	10	
1.150	<10	400	0.982	10	
1.096	<10	222			
1.086	<10	330			
1.047	<10	411			
1.041	<10	312			
0.9107	<10	402			
0.9029	<10	510			
0.8939	<10	213			
0.8902	<10				
0.8819	<10	431			
0.8784	<10	332			
0.8479	<10	422, 223			
0.8331	<10	303			
0.8234	<10	521			

[a] The detail of these two lines can be seen in Ref. 9

diffraction lines from powder diffraction file is shown in Table 5. Another reflection of metapyrophanite that should be present in the photograph is that with the interplanar spacing $d_o = 2.79$ Å. Perhaps owing to the relatively intense background of the Guinier-Hägg photograph, the line appears very weak. Table 6 shows the JCPDS powder diffraction data of niobian-rutile and pyrophanite.

The results of the two refinements, using 13 lines of niobian-rutile and 8 lines of pyrophanite indicated that niobian-rutile and pyrophanite are crystals of tetragonal and hexagonal systems respectively. The unit cell dimensions of the two minerals are presented in Table 7.

TABLE 7: THE UNIT CELL DIMENSIONS Å OF NIOBIAN-RUTILE AND PYROPHANITE

	This experiment		JCPDS powder data	
	Niobian-rutile Tetragonal system	Pyrophanite Hexagonal system	Niobian-rutile Tetragonal system	Pyrophanite Hexagonal system
a	4.5919(5)	5.092(1)	4.606	5.137
b	2.9583(4)	14.099(8)	2.982	14.29

TABLE 8: POWDER DIFFRACTION DATA OF A NIOBIUM-TANTALUM SAMPLE CONSISTING OF ILMENORUTILE AND CASSITERITE

Niobium-tantalum sample				Ilmenorutile Tetragonal system			Cassiterite[a] Tetragonal system		
I/I_1	$S-S_o$mm	d Å	$\sin^2\theta_o$	$\sin^2\theta_c$	d_c	*hkl*	$\sin^2\theta_o$	*hkl*	I/I_1
10	42.37	3.667	.04413						
70	46.47	3.348	.05292				.05289	110	100
100	47.54	3.274	.05534	.05536	3.274	110			
16	52.57	2.967	.06738						
60	59.20	2.643	.08492				.08489	101	84
50	62.54	2.506	.09445	.09446	2.506	101			
5	65.87	2.384	.10440						
15	66.33	2.368	.10581				.10581	200	28
28	67.88	2.316	.11062	.11072	2.315	200			
11	71.46	2.205	.12208	.12214	2.204	111			
<5	76.33	2.070	.13844	.13840	2.071	210			
48	90.51	1.763	.19082				.19073	211	60
52	94.15	1.700	.20531	.20518	1.701	211			
16	95.71	1.674	.21164				.21159	220	35
34	98.08	1.637	.22139	.22143	1.637	220			
11	101.11	1.592	.23408				.23407	002	15
10	108.15	1.498	.26448				.26449	310	20
10	108.60	1.492	.26647[b]	.26714	1.490	002			
7	110.95	1.464	.27691	.27679	1.464	310			
11	113.19	1.438	.28698				.28699	112	16
11	115.31	1.414	.29660				.29662	301	17
<5	119.48	1.371	.31580	.31590	1.371	301			
5	120.77	1.358	.32180[b]	.32250	1.356	112			
<5	124.59	1.322	.33975				.33987	202	11
<5	137.55	1.215	.40224[b]	.40554	1.210	212	.40232	321	14
<5	146.41	1.153	.44596[b]	.44287	1.158	400	.44581	222	14
<5	147.37	1.147	.45073						
<5	152.34	1.117	.47548				.47593	330	9
10	156.67	1.093	.49709				.49821	312	15

[a] data from powder photograph in Fig. 4 and the result of refinement in Table 11
[b] not used in the refinement

Ilmenorutile.[12] This mineral is generally called niobian-rutile. Analysis of the powder diffraction photograph in Fig. 3 showed that the sample consists of ilmenorutile mixed with quite a large amount of cassiterite. Ilmenorutile $[Fe_{x/3}(Nb, Ta)_{2x/3}Ti_{1-x}O_2]$ and strüverite[13] $[Fe_{x/3}(Ta, Nb)_{2x/3}Ti_{1-x}O_2]$ are two minerals which are very much alike. They differ only by the percentage of niobium or tantalum presented. The powder diffraction data from Fig. 3a and the results of the refinement are shown in Table 8. Comparing Table 8 and Table 9 which shows the differences of strüverite and ilmenorutile from the JCPDS powder diffraction file, it was obvious that the sample consists of ilmenorutile and cassisterite.

TABLE 9: COMPARISON OF POWDER DATA FROM POWDER PHOTOGRAPH OF FIG. 3 WITH THE JCPDS POWDER DATA OF TANTALIAN-RUTILE AND NIOBIAN-RUTILE

Tantalian-rutile card no. 17–543 $Fe_{x/3}(Ta, Nb)_{2x/3}Ti_{1-x}O_2$ (Strüverite)			Ilmenorutile Data from Fig. 3			Niobian-rutile card no. 16–934 $Fe_{x/3}(Nb, Ta)_{2x/3}Ti_{1-x}O_2$ (Ilmenorutile)		
d Å	I/I_1	*hkl*	d Å	I/I_1	*hkl*	d Å	I/I_1	*hkl*
3.28	100	110	3.274	100	110	3.28	100	110
2.52	90	101	2.506	50	101	2.51	90	101
2.32	40	200	2.316	28	200	2.32	30	200
2.21	30	111	2.205	11	111	2.20	50	111
2.08	20	210	2.070	<5	210	2.07	20	210
1.707	100	211	1.700	52	211	1.702	100	211
1.668	<10	?						
1.642	60	220	1.637	34	220	1.638	60	220
1.497	20	002	1.492	10	002	1.494	20	002
1.469	30	310	1.464	7	310	1.466	30	310
1.376	40	301	1.371	<5	301	1.373	40	301
1.361	30	112	1.358	5	112	1.357	30	112
1.258	20	202	1.215	<5	212	1.254	10	202
1.184	30	321				1.181	20	321
1.162	10	400	1.153	<5	400	1.158	10	400
1.109	20	222				1.103	20	222
1.096	10	330				1.093	10	330
1.055	10	411				1.052	10	411
1.050	10	312				1.046	10	312
1.038	10	420				1.038	10	420

The tetragonal unit cell dimensions of ilmenorutile obtained from the refinement using 9 reflections compared with those of strüverite and ilmenorutile from the JCPDS powder diffraction files are presented in Table 10.

TABLE 10: THE TETRAGONAL UNIT CELL DIMENSIONS Å OF NIOBIAN-RUTILE AND TANTALIAN-RUTILE

Niobian-rutile (Ilmenorutile) This experiment	Tantalian-rutile (Strüverite) Card no. 17–543	Niobian-rutile (Ilmenorutile) Card no. 16–934
a 4.6300(4)	4.645	4.635
c 2.981(1)	2.999	2.986

Cassiterite. One of the samples was found to be cassiterite, mixed with a small quantity of other minerals (Fig. 4). Since cassiterite is always present in most samples in the niobium-tantalum family we studied, it would be interesting to analyze this mineral itself by using the same Guinier-Hägg camera in order to obtain data for the camera of the same type. This also serves to check the accuracy of the camera.

TABLE 11: POWDER DIFFRACTION DATA OF A SAMPLE CONSISTING OF CASSITERITE AND SOME UNKNOWN MINERALS COMPARED WITH THE JCPDS POWDER DATA OF CASSITERITE

Mineral sample							Cassiterite card no. 21–1250		
I/I_1	$S-S_o$mm	d_o Å	$\sin^2\theta_o$	$\sin^2\theta_c$	d_c Å	*hkl*	d Å	I/I_1	*hkl*
							3.35	100	110
<5	42 34	3.671	.04404				2.644	80	101
100	46.47	3.349	.05289	.05289	3.349	110	2.369	25	200
9	47.46	3.281	.05513				2.309	6	111
<5	50.31	3.098	.06180				2.120	2	210
13	52.45	2.975	.06705				1.765	65	211
<5	54.28	2.877	.07170				1.675	16	220
84	59.20	2.644	.08489	.08496	2.643	101	1.593	8	002
17	62.16	2.522	.09331				1.498	14	310
28	66.34	2.368	.10581	.10579	2.368	200	1.439	18	112
7	68.14	2.308	.11141	.11141	2.308	111	1.415	16	301
<5	74.52	2.118	.13224	.13224	2.118	210	1.322	8	202
<5	75.77	2.085	.13650				1.215	12	321
60	90.49	1.764	.19073	.19075	1.764	211	1.184	4	400
35	95.70	1.675	.21159	.21158	1.675	220	1.155	8	222
15	101.11	1.592	.23407	.23404	1.592	002	1.117	4	330
18	108.15	1.498	.26449	.26447	1.498	310	1.092	8	312
16	113.19	1.438	.28699	.28694	1.438	112	1.081	8	411
17	115.31	1.414	.29662	.29653	1.415	301	1.059	4	420
11	124.61	1.321	.33987	.33983	1.321	202	1.036	4	103
14	137.56	1.214	.40232	.40232	1.214	321	0.9505	8	402
<5	141.82	1.184	.42328	.42315	1.184	400	.9291	4	510
14	146.37	1.154	.44581	.44562	1.154	222	.9143	4	332
9	152.42	1.117	.47593	.47605	1.116	330	.9081	8	501
15	156.88	1.091	.49821	.49851	1.091	312	.8819	8	422
							.8814	6	303
							.8480	6	521
							.8375	2	440
							.8261	4	323
							.8125	2	530
							.8026	6	512

Cassiterite has already been studied in detail by Swanson and Tatge[14] using diffractometer. By analyzing the 24 lines in the powder diffraction pattern in Fig. 4. and comparing with the data from the powder diffraction file, it was found that 17 reflections belong to cassiterite. The remaining 7 reflections probably belong to more than two kinds of other minerals. Since only very few lines were present, they were not investigated further. The result of the refinement using 17 diffraction lines comparing with those from powder diffraction files were shown in Table 11. The unit cell dimensions of this mineral are very close to those obtained by Swanson and Tatge as shown in Table 12.

TABLE 12: THE TETRAGONAL UNIT CELL DIMENSIONS OF CASSITERITE FROM THIS INVESTIGATION COMPARING WITH SWANSON AND TATGE WORK

	Unit cell dimensions (Å) This investigation	Unit cell dimensions (Å) Swanson and Tatge[14]
a	4.7366(3)	4.738
c	3.1845(3)	3.188

Although data of Swanson and Tatge were obtained by diffractometer, the values of d spacings were very close to those obtained in this experiment. The intensity recorded in this experiment is the peak intensity which, to a certain extent, gives not significantly different results. However there are some other minerals mixed in the cassiterite sample, presumably these are columbite-tantalite and other minerals.

Conclusions and Discussions

This work was to identify the minerals in the niobium-tantalum family which may be contained in the minerals obtained from various mines, and to obtain X-ray diffraction data of these minerals in detail. The X-ray powder diffraction method by XDC–700 camera is fairly suitable for mineral identification and also is one of the accurate methods for obtaining the powder data. The Guinier-Hägg focussing

TABLE 13: MINERALS FOUND IN THE NIOBIUM-TANTALUM SAMPLES BY THIS INVESTIGATION

Substance	Mineral name	Chemical formula	Crystal system	Space group	Card no
Iron Manganese Niobium Tantalum Oxide	Columbite-Tantalite	$(Fe, Mn) (Nb, Ta)_2O_6$	Orthorhombic	Pcan(No. 60)	16–337
Iron Niobium Tantalum Titanium Oxide	Niobianrutile	$Fe_x^{2+}(Nb, Ta)_{2x}Ti_{1-x}O_2$	Tetragonal	–	11–396
Iron Niobium Tantalum Titanium Oxide	Ilmenorutile	$Fe_{x/3}(Nb, Ta)_{2x/3}Ti_{1-x}O_2$	Tetragonal	–	16–934
Manganese Titanium Oxide	Pyrophanite	$MnTiO_3$	Hexagonal	$R\bar{3}$ (No. 148)	12–435
Manganese Meta Titanate	Metapyro-planite	$MnO.TiO_2$	Hexagonal	$R\bar{3}$ (No. 148)	2–846
Tin Oxide	Cassiterite	SnO_2	Tetragonal	$P4_2/mnm$ (No. 136)	21–1250

camera is very useful for this work because it needs only a small amount of sample. Quantitative analysis of the mineral components was only considered roughly by looking at the intensity of the diffraction lines in the photographs and the number of reflections.

The identification of these minerals was rather complicated, since data from the powder photograph are those of many components of mineral. This work was done by comparing with the simulated X-ray powder patterns[15] which used a "computer and plotter"* to plot the powder pattern for Guinier-Hägg camera using data of the minerals in niobium-tantalum family from the JCPDS powder diffraction files.

From the experiment, it was found that at least 2 kinds of minerals are found in a sample. Some minerals have very similar powder patterns so that careful comparison must be done especially when there is data of low reliability from the JCPDS powder diffraction file. Table 13 gives the results of identification of the minerals contained in the samples. Refinement by least-squares method gives the more accurate values of the unit cell dimensions and also confirm the reliability of powder data from this experiment.

From the samples studied, it was found that columbite-tantalite was present in many samples. However these are more or less mixed with cassiterite and/or some other minerals. Four of the samples consist of large amount of columbite-tantalite, while it is slightly mixed in some other samples.

For niobian-rutile and tantalian-rutile, there is an interesting point worth mentioning, namely there are 3 kinds which are very much alike and their structures have not been investigated.

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*The simulated pattern calculation was done with the IBM 1800 computer at the Institute of Chemistry, Uppsala University, Sweden

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บทคัดย่อ

การศึกษาส่วนประกอบของแร่ในตระกูลไนโอเบียม-แทนทาลัม จากเหมืองบางแห่งในประเทศไทย ได้กระทำโดยวิธีการเลี้ยวเบนรังสีเอ๊กซ์ของผลึกผง พบว่ามีแร่โคลัมไบท์-แทนทาไลท์ ในโอเบียนรูไทล์ และอิลเมโนรูไทล์ ส่วนใหญ่จะมีแร่แคสสิเทอไรท์ปนอยู่ด้วย ขนาดของหน่วยเซลล์ของแร่เหล่านี้ทำการเกลา โดยวิธีกำลังสองน้อยที่สุด ข้อมูลการเลี้ยวเบนของผลึกผงจากภาพถ่ายด้วยกล้องกีเนียร์-เฮก ชนิดปรับโฟกัส จัดแสดงในรูปตาราง ภาพถ่ายเหล่านี้สามารถใช้เป็นมาตรฐานในการพิสูจน์เอกลักษณ์ได้รวดเร็ว และแม่นยำขึ้น