

# Powder Diffraction Studies of SrNb<sub>2</sub>O<sub>6</sub> and SrNb<sub>6</sub>O<sub>16</sub>

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The crystal structure of the monoclinic modification of SrNb<sub>2</sub>O<sub>6</sub> was studied with Guinier-Hägg X-ray powder diffraction data. The cell dimensions are  $a = 7.7223(7)$  Å,  $b = 5.5944(5)$  Å,  $c = 10.9862(7)$  Å and  $\beta = 90.372(5)^\circ$ . The space group is  $P2_1/c$ . The structure was refined by the Rietveld full-profile technique. A comparison was made with the isostructural orthorhombic CaTa<sub>2</sub>O<sub>6</sub>. An orthorhombic strontium/niobium oxide with unit cell dimensions  $a = 3.9563(3)$  Å,  $b = 10.1889(8)$  Å and  $c = 14.794(1)$  Å was studied with Guinier-Hägg data from a mixed pattern. It is shown that the compound is isostructural with NaNb<sub>6</sub>O<sub>15</sub>F and has the composition SrNb<sub>6</sub>O<sub>16</sub>.

The binary oxide system SrO-Nb<sub>2</sub>O<sub>5</sub> contains a large number of phases that can be denoted by the general formula  $X\text{SrO} \cdot Y\text{Nb}_2\text{O}_5$ . Goldschmidt<sup>1</sup> detected, by means of powder patterns, four phases of approximate compositions  $(X/Y) = (1/1)$ ,  $(2/3)$ ,  $(1/3)$  and  $(1/12)$ . Francombe<sup>2</sup> reported a phase of composition  $(2/5)$ ; Whiston and Smith<sup>3</sup> a phase  $(3/5)$ . Appendino and Burlando<sup>4</sup> determined unit cell dimensions for the phases  $(6/1)$ ,  $(5/2)$  and  $(2/1)$ . Furthermore, Appendino and Montorsi<sup>5</sup> reported a powder diffraction pattern from a phase for which they proposed the composition  $(3/8)$ . The published pattern was not indexed, but we were able to index it by an orthorhombic unit cell  $a = 3.962$  Å,  $b = 10.177$  Å and  $c = 14.760$  Å with a De Wolff figure of merit  $M_{20} = 20$ ;<sup>6</sup> furthermore, the published pattern showed strong similarities with that of NaNb<sub>6</sub>O<sub>15</sub>F.<sup>7</sup> This indicated not only that the composition of the phase is  $(1/3)$ , but also that it is isostructural with NaNb<sub>6</sub>O<sub>15</sub>F. It should be noted that the phase  $(1/3)$  reported by Goldschmidt<sup>1</sup> is of the tetragonal bronze type. Therefore, we decided to synthesize the orthorhombic phase and check the structural hypothesis by a Rietveld profile analysis of an X-ray Guinier

powder pattern. As discussed below, however, we were only able to prepare a two-phase sample of the orthorhombic phase and a monoclinic modification of SrNb<sub>2</sub>O<sub>6</sub>. In order to facilitate the study of the two-phase sample, the monoclinic SrNb<sub>2</sub>O<sub>6</sub> phase was first investigated separately.

Two modifications of SrNb<sub>2</sub>O<sub>6</sub> and the conditions of reversible transformation of the two phases into one another have been described by Brusset *et al.*<sup>8</sup> A tetragonal high-temperature modification having the potassium tungsten

Table 1. Crystal data.

Stoichiometry	SrNb <sub>2</sub> O <sub>6</sub>	SrNb <sub>6</sub> O <sub>16</sub>
Space group	$P2_1/c$	$Pmm2$
Z	4	2
F.W.	369.4	901.06
$a/\text{Å}$	7.7223(7)	3.9563(3)
$b/\text{Å}$	5.5944(5)	10.1889(8)
$c/\text{Å}$	10.9862(7)	14.794(1)
$\beta/^\circ$	90.372(5)	
$V/\text{Å}^3$	474.6	596.4
$d\text{-calc}/\text{g cm}^{-3}$	5.17	5.02
Cell figures of merit:		
$M_{20}$	29	33
$F_{77}$	34 (0.010, 233)	–
$F_{82}$	–	38 (0.010, 216)

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Table 2. X-ray powder diffraction pattern of monoclinic SrNb<sub>2</sub>O<sub>6</sub>.

(hkl)	2θ-obs	2θ-calc	Δ(2θ)	d-obs	l-obs	(hkl)	2θ-obs	2θ-calc	Δ(2θ)	d-obs	l-obs
(002)	16.141	16.123	0.018	5.487	81	(2̄24)	52.193	52.204	-0.011	1.7511	1053
(011)	17.794	17.777	0.017	4.981	451	(224)	52.403	52.414	-0.011	1.7446	617
(110)	19.589	19.579	0.010	4.528	86	(412)		52.924	0.031		
(1̄02)	19.793	19.758	0.035	4.482	87	(025)	52.955	52.950	0.005	1.7277	77
(102)	19.911	19.880	0.031	4.456	45	(1̄32)	53.144	53.139	0.005	1.7220	69
(1̄11)		21.167	0.034			(132)		53.191	-0.053		
(111)	21.201	21.225	-0.024	4.187	149	(033)	55.239	55.232	0.007	1.6616	1687
(012)	22.667	22.668	-0.001	3.9197	89	(231)		55.273	-0.034		
(200)	23.030	23.016	0.014	3.8587	558	(206)	55.642	55.650	-0.018	1.6505	182
(2̄02)	28.169	28.141	0.023	3.1654	218	(413)	56.415	56.428	-0.013	1.6297	1174
(202)	28.331	28.317	0.014	3.1476	747	(232)	57.297	57.280	0.017	1.6067	735
(013)	29.118	29.122	-0.004	3.0643	4557	(3̄15)		57.324	-0.027		
(2̄11)		29.190	-0.072			(315)	57.693	57.695	-0.002	1.5966	131
(1̄13)	31.337	31.325	0.012	2.8522	207	(2̄16)		57.948	0.042		
(113)	31.445	31.445	0.000	2.8426	85	(420)	57.990	58.001	-0.011	1.5891	725
(020)	31.962	31.970	-0.008	2.7979	1180	(404)	58.174	58.186	-0.012	1.5845	179
(004)	32.576	0.008	2.7458	321	(2̄25)	58.349	58.350	-0.001	1.5802	175	
(212)		32.603	-0.019			(404)		58.577	0.013		
(104)	34.575	34.563	0.012	2.5921	133	(225)	58.590	58.594	-0.004	1.5743	350
(104)	34.727	34.709	0.018	2.5812	54	(4̄21)		58.614	-0.024		
(014)	36.415	36.413	0.002	2.4653	224	(034)	59.903	59.906	-0.003	1.5429	77
(213)	37.541	37.543	-0.002	2.3939	260	(026)	60.376	60.373	-0.003	1.5319	210
(1̄22)	37.880	37.865	0.015	2.3732	166	(422)	60.532	60.526	0.006	1.5283	221
(122)		37.933	-0.053			(233)		60.545	-0.013		
(310)	38.473	38.466	0.007	2.3380	249	(233)	60.684	60.689	-0.005	1.5249	231
(3̄02)		38.496	-0.023			(414)		60.709	-0.025		
(302)	38.688	38.696	-0.009	2.3255	34	(422)		60.717	-0.037		
(220)	39.765	39.760	0.005	2.2650	76	(134)		61.236	0.060		
(2̄04)	40.132	40.135	-0.003	2.2451	420	(017)	61.296	61.296	0.000	1.5111	848
(204)	40.396	40.393	0.003	2.2310	275	(330)		61.333	-0.043		
(023)	40.543	40.550	-0.007	2.2233	212	(1̄26)	61.592	61.605	-0.013	1.5045	77
(221)		40.601	-0.058			(117)		62.506	0.018		
(1̄23)	42.236	42.228	0.008	2.1380	195	(502)	62.524	62.527	-0.003	1.4843	68
(222)	43.217	43.225	-0.008	2.0917	979	(423)	63.650	63.666	-0.016	1.4608	87
(214)	43.624	43.639	-0.015	2.0731	44	(035)		65.611	0.022		
(015)	44.252	44.253	-0.001	2.0452	205	(226)	65.633	65.634	-0.001	1.4213	149
(1̄15)	45.802	45.791	0.011	1.9795	204	(217)	66.234	66.220	0.014	1.4099	587
(313)	45.909	45.884	0.025	1.9751	218	(217)	66.537	66.538	-0.001	1.4042	301
(115)		45.936	-0.027			(1̄35)		66.801	0.035		
(024)	46.276	46.290	-0.014	1.9603	696	(040)	66.836	66.839	-0.003	1.3986	250
(400)	47.016	47.033	-0.017	1.9312	1244	(3̄23)		66.873	0.037		
(2̄23)		47.053	-0.037			(041)	67.467	67.450	0.017	1.3871	142
(124)	47.791	47.791	0.000	1.9017	83	(513)	67.757	67.742	0.015	1.3819	66
(3̄04)	48.242	48.260	-0.018	1.8849	66	(424)	67.953	67.945	0.008	1.3783	230
(304)	48.598	48.594	0.004	1.8719	74	(008)	68.265	68.241	0.024	1.3728	134
(006)	49.753	49.757	-0.004	1.8311	244	(424)		68.304	-0.039		
(402)	49.912	49.931	-0.019	1.8257	172	(1̄41)		68.668	0.024		
(410)		49.934	-0.022			(141)	68.692	68.691	0.001	1.3653	44
(130)	50.289	50.295	-0.006	1.8129	177	(406)	71.157	71.141	0.016	1.3240	147
(2̄15)		50.322	-0.033			(043)		72.252	0.046		
(215)	50.598	50.591	0.007	1.8025	232	(036)		72.256	0.042		
(4̄11)		50.613	-0.015			(2̄41)	72.298	72.287	0.011	1.3058	532
(322)	50.873	50.878	-0.005	1.7934	103	(514)		72.326	-0.028		
(314)		51.110	0.031			(241)		72.331	-0.033		
(1̄06)	51.141	51.155	-0.014	1.7846	80	(416)		72.899	0.029		
(106)	51.310	51.315	-0.005	1.7792	64	(203)	72.928	72.902	0.026	1.2961	183
(032)	51.719	51.727	-0.008	1.7661	123						

Table 3. Fractional atomic coordinates in SrNb<sub>2</sub>O<sub>6</sub> with e.s.d.s, as calculated from the least-squares refinement, in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Sr	0.2523(7)	0.5360(10)	0.0393(3)
Nb(1)	0.0143(6)	0.0294(17)	0.1448(4)
Nb(2)	0.5232(6)	0.4698(16)	0.6428(4)
O(1)	0.044(4)	0.228(6)	0.975(3)
O(2)	0.456(4)	0.262(7)	0.467(3)
O(3)	0.070(4)	0.376(5)	0.206(3)
O(4)	0.454(4)	0.129(5)	0.701(3)
O(5)	0.258(4)	0.963(5)	0.149(2)
O(6)	0.758(5)	0.149(4)	0.116(2)

and illustrates clearly the similarity between the SrNb<sub>2</sub>O<sub>6</sub> and the CaTa<sub>2</sub>O<sub>6</sub> structures.

Appendino and Burlando,<sup>4</sup> however, reported powder diffraction data for the low-temperature phase of SrNb<sub>2</sub>O<sub>6</sub> and indexed the pattern by an orthorhombic cell. This can be understood from the fact that the monoclinic angle deviates from 90° by only a few tenths of a degree and that the diffraction data were obtained by the Debye-Scherrer method. As there are strong reasons to believe that Guinier-Hägg photographs measured by an automatic film scanner instrument should give more accurate data, we decided to refine the unit cell dimensions and make a profile refinement of the structure using this type of

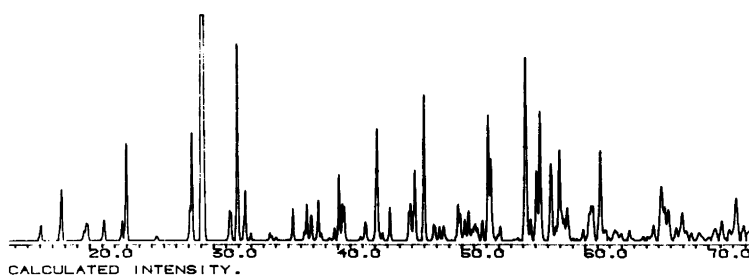
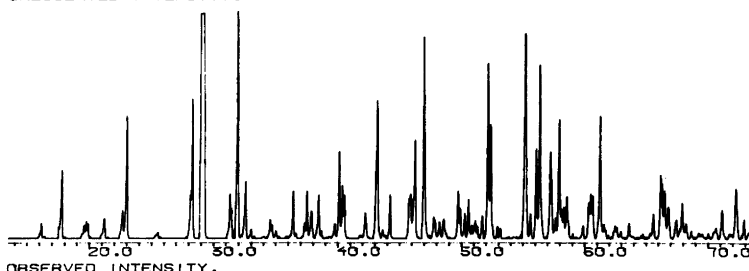


Fig. 1. Observed and calculated X-ray powder diffraction intensities for monoclinic SrNb<sub>2</sub>O<sub>6</sub> as a function of 2θ. Only the lowest third of the tallest peak at 2θ = 29° is shown on the figure.



bronze structure is obtained if the sample is heated 96 h at 1450°C. At lower temperatures, a monoclinic pseudoorthorhombic modification, isostructural with orthorhombic CaTa<sub>2</sub>O<sub>6</sub>, is formed.<sup>9</sup> In the paper by Brusset *et al.*,<sup>8</sup> approximate cell dimensions and an electron projection map of the monoclinic structure, but no atomic coordinates, are given. The electron density projection is calculated from single-crystal film data

data. In cases of very slight monoclinic splitting of reflections, there are also usually some advantages in Guinier over Debye-Scherrer or powder diffractometer methods because of the smaller half-widths of the diffraction lines\*.

## Experimental

*SrNb<sub>2</sub>O<sub>6</sub>*. The sample of SrNb<sub>2</sub>O<sub>6</sub> used in this investigation was prepared from Nb<sub>2</sub>O<sub>5</sub> (Optipur) heated 48 h at 1000°C and SrCO<sub>3</sub> (Mallinckrodt, 99.7%). After preliminary decomposition, 20 h at 800°C, a pressed disk of stoichiometric amounts of SrO and Nb<sub>2</sub>O<sub>5</sub> was heated 48 h at 1200°C on a platinum foil.

\*After submitting the manuscript of this article, the authors became aware of a structure determination of SrNb<sub>2</sub>O<sub>6</sub> based on single-crystal data<sup>14</sup>. Our results agree fairly well with those reported in that paper.

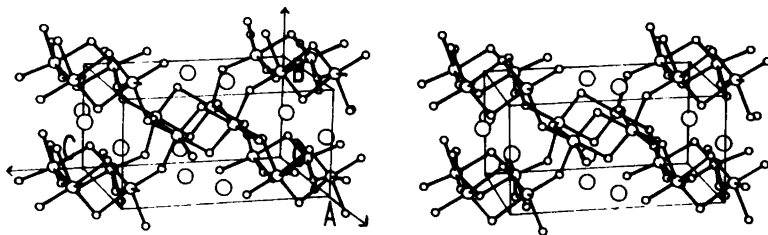


Fig. 2. Stereo view of monoclinic  $\text{SrNb}_2\text{O}_6$ . Large circles = Sr, medium circles = Nb and small circles = O.

$\text{SrNb}_6\text{O}_{16}$ . Pressed disks of SrO as described above, and  $\text{Nb}_2\text{O}_5$  in the molar ratio 2:5 were heated for 4 d at  $1200^\circ\text{C}$  on platinum foils. An X-ray powder diffraction pattern from the product showed only the existence of the phase  $2\text{SrO} \cdot 5\text{Nb}_2\text{O}_5$ .<sup>4</sup> All attempts to prepare  $3\text{SrO} \cdot 8\text{Nb}_2\text{O}_5$  (or  $\text{SrO} \cdot 3\text{Nb}_2\text{O}_5$ ) directly from SrO and  $\text{Nb}_2\text{O}_5$  by heating in the ranges  $850^\circ\text{C}$  to  $1000^\circ\text{C}$  for 4 to 10 d failed, however.

According to Appendino and Burlando,<sup>4</sup> the phase  $3\text{SrO} \cdot 8\text{Nb}_2\text{O}_5$  can be obtained by decomposing  $2\text{SrO} \cdot 5\text{Nb}_2\text{O}_5$  at temperatures below  $1100^\circ\text{C}$ . Although we tried to heat  $2\text{SrO} \cdot 5\text{Nb}_2\text{O}_5$  at various temperatures between  $800^\circ\text{C}$  and  $1050^\circ\text{C}$  for up to 4 d, we were not able to decompose  $2\text{SrO} \cdot 5\text{Nb}_2\text{O}_5$  without addition of some amount of  $\text{Nb}_2\text{O}_5$ . After 4 d of heating at  $1000^\circ\text{C}$  of  $2\text{SrO} \cdot 5\text{Nb}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  in the molar ratio 3:1, a Guinier powder photograph showed lines from the monoclinic modification of  $\text{SrO} \cdot \text{Nb}_2\text{O}_5$ <sup>4</sup> and from the phase which was assigned the formula  $3\text{SrO} \cdot 8\text{Nb}_2\text{O}_5$  by Appendino and Montorsi.<sup>5</sup> As shown in the present work, however, the latter phase is isostructural with  $\text{NaNb}_6\text{O}_{15}\text{F}^7$  and has the composition  $\text{SrO} \cdot 3\text{Nb}_2\text{O}_5$ . Although the vast majority of the diffraction lines represent the phases  $\text{SrO} \cdot 3\text{Nb}_2\text{O}_5$  and  $\text{SrO} \cdot \text{Nb}_2\text{O}_5$ , a small contribution from  $\text{Nb}_2\text{O}_5$  can be found in the pattern. The mixed Guinier pattern is shown in Table 5.

**Powder diffraction photographs.** X-ray powder diffraction photographs were taken in a subtraction-geometry Guinier-Hägg focusing camera of 80 mm diameter, with strictly monochromatized  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ).<sup>10</sup> The atmosphere in the camera housing during the exposures was dry air at room temperature. Single coated film (CEA Reflex 15) was used so that a back-layer profile would be avoided and the background diminished, thus improving the signal-to-noise ratio. Finely powdered silicon

( $a = 5.430880 \pm 35 \text{ \AA}$  at  $25^\circ\text{C}$ )<sup>11</sup> was added as internal  $\theta$  standard in the samples used for least-squares refinement of unit cell dimensions. Step-scan intensities used for Rietveld profile refinements were evaluated from photographs taken without silicon but using lines from the samples as  $\theta$  standards. The films were measured by an automatic single-beam microdensitometer.<sup>12</sup> The slit opening of the collimator was  $0.040 \times 2.0 \text{ mm}$ ; the step length  $0.020 \text{ mm}$ , corresponding to  $0.0143^\circ$  in  $2\theta$ . Trial runs with a collimator slit opening of  $0.020 \times 2.0 \text{ mm}$  were found to give unacceptably high noise levels. (The lower limit of the slit opening in the step-scan direction should depend on the grain size of the film emulsion.) The  $2\theta$  range used for profile analysis of  $\text{SrNb}_2\text{O}_6$  was  $15^\circ \leq 2\theta \leq 73.4^\circ$ , and that for  $\text{SrNb}_6\text{O}_{16}$ ,  $10^\circ \leq 2\theta \leq 74.6^\circ$ .

Table 4. Interatomic distances ( $\text{\AA}$ ) in  $\text{SrNb}_2\text{O}_6$ , with e.s.d. in parentheses.

Sr—O(1)	2.46(4)
O(1)'	2.65(4)
O(2)	2.43(4)
O(2)'	2.59(4)
O(3)	2.49(3)
O(4)	2.53(3)
O(5)	2.68(3)
O(6)	2.46(2)
Nb(1)—O(1)	2.00(4)
O(1)'	2.19(3)
O(3)	1.96(3)
O(3)'	2.10(3)
O(5)	1.92(3)
O(6)	2.11(4)
Nb(2)—O(2)	1.94(4)
O(2)'	2.31(3)
O(4)	1.94(3)
O(4)'	2.08(3)
O(5)	2.08(3)
O(6)	1.96(3)

Table 5. X-ray powder diffraction pattern of SrNb<sub>6</sub>O<sub>16</sub> (A) and SrNb<sub>2</sub>O<sub>6</sub> (B) in the molar ratio 5:1. Small intensity contributions from Nb<sub>2</sub>O<sub>5</sub> (C) are also present in the mixed pattern. Some reflections can be indexed by more than one phase and asterisks are therefore used to denote reflections which may have negligible intensities according to Rietveld refinements.

2θ-obs	A	2θ-calc B	C	d-obs	l-obs	A	(hkl) B	C
10.511	10.534			8.410	112	(011)		
11.947	11.954			7.402	60	(002)		
16.104		16.122		5.500	48		(002)	
17.250			17.367	5.137	48			( $\bar{4}$ 01)
17.760		17.777		4.990	160		(011)	
19.992	19.987			4.438	188	(013)		
21.156	21.158			4.196	65	(022)		
22.467	22.455			3.9542	2446	(100)		
23.039		23.016		3.8573	158		(200)	
23.757			23.758	3.7422	301			(110)
24.043	24.042			3.6984	689	(004)		
24.442			24.463	3.6389	133			( $\bar{1}$ 05)
24.868	24.861			3.5776	664	(111)		
25.538	25.512		25.578	3.4852	352	(102)		( $\bar{5}$ 05)
			25.587					(012)
			26.549	3.3520	56			(005)
26.571				3.3102	2821	(031)		
26.912	26.913					(112)		
	26.993							
28.343		28.317		3.1462	224		(202)	
28.548	28.543			3.1242	160	(120)		
29.149	29.187	29.122		3.0612	2781	(121)*	(013)	
29.826	29.828			2.9932	1809	(024)		
	30.180					(005)		
30.249	30.236			2.9522	730	(113)		
31.050	31.044			2.8779	198	(122)		
31.465	31.458			2.8409	1283	(015)		
31.968	31.970	31.970		2.7973	1294	(033)	(020)	
32.242			32.313	2.7742	45			( $\bar{5}$ 11)
32.572		32.576		2.7469	70		(004)	
33.136	33.130			2.7014	893	(104)		
33.953	33.936			2.6382	58	(123)		
35.329	35.326			2.5385	1582	(131)		
36.033			35.970	2.4906	29			(602)
			36.107					(707)
36.415	36.408	36.413		2.4653	165	(006)	(014)	
36.908	36.907			2.4335	74	(132)		
37.318	37.306			2.4077	106	(042)		
37.657	37.655			2.3868	1056	(124)		
37.940	37.942			2.3696	62	(105)		
		38.466					(310)	
38.488		38.496		2.3371	49		( $\bar{3}$ 02)	
38.895			38.871	2.3136	74			( $\bar{9}$ 03)
			38.925					(413)
38.993	38.995			2.3080	57	(115)		
39.416	39.421			2.2842	101	(133)		
40.162		40.135		2.2435	139		( $\bar{2}$ 04)	
40.402	40.397	40.393		2.2307	338	(035)	(204)	
		40.550					(023)	
40.603	40.616	40.601		2.2201	203	(026)	( $\bar{2}$ 21)*	
		40.665					(221)	(cont.)

2θ-obs	A	2θ-calc B	C	d-obs	l-obs	A	(hkl) B	C
42.238		42.228		2.1380	27		( $\bar{1}$ 23)	
43.107	43.084	43.225		2.0968	763	(044)	(222)	
43.701	43.706			2.0697	377	(017)		
43.979	43.979			2.0572	72	(142)		
44.267		44.253		2.0445	112		(015)	
44.866	44.863			2.0186	87	(051)		
45.844	45.835			1.9778	1626	(200)		
46.248	46.266	46.290		1.9614	233	(201)*	(024)	
46.701	46.705			1.9434	170	(135)		
	46.741					(210)		
46.929	46.900			1.9345	267	(126)		
47.028	47.035	47.033		1.9307	309	(045)*	(400)	
		47.053					(223)	
47.509			47.462					( $\bar{1}$ 18)
			47.527	1.9123	151			(40 $\frac{1}{2}$ )
			47.529					(020)
48.285	48.285			1.8833	291	(053)		
48.414	44.424			1.8786	159	(212)		
49.123	49.116			1.8532	543	(144)		
49.639	49.614			1.8351	136	(203)		
	49.678					(117)		
49.783	49.791	49.757		1.8301	215	(221)*	(006)	
50.734	50.730			1.7980	363	(151)		
50.829	50.843			1.7949	211	(037)		
51.237	51.236			1.7815	76	(136)		
51.523	51.544			1.7723	67	(046)		
51.948	51.923			1.7588	54	(152)		
52.199	52.209	52.204		1.7510	302	(127)*	( $\bar{2}$ 24)	
52.425	52.412	52.414		1.7439	331	(204)	(224)	
52.598	52.607			1.7386	590	(028)		
52.972	52.972			1.7272	102	(223)		
	53.871					(153)		
53.927	53.951			1.6989	2284	(060)		
	53.955					(231)		
54.652	54.643			1.6780	1538	(055)		
55.179		55.232		1.6632	430		(033)	
55.652	55.649			1.6502	504	(224)		
56.236	56.246			1.6345	547	(137)		
56.410		56.428		1.6298	237		(413)	
	56.625					(038)		
56.662	56.650			1.6232	340	(215)		
	56.674					(019)		
	56.900					(146)		
56.944	56.972			1.6158	270	(233)		
57.293		57.280		1.6068	99		( $\bar{2}$ 32)	
		57.324					(315)	
57.894	57.894			1.5915	574	(128)		
59.140	59.159			1.5609	391	(160)		
59.813	59.811			1.5450	478	(155)		
60.534	60.519			1.5283	178	(242)		
61.274		61.296		1.5116	140		(017)	
	61.686					(138)		
61.737	61.733			1.5014	217	(119)		

(cont.)

2θ-obs	2θ-calc			d-obs	l-obs	(hkl)		
	A	B	C			A	B	C
62.309	62.288			1.4889	49	(243)		
62.737	62.722			1.4798	540	(235)		
	62.745					(039)		
63.347	62.754			1.4670	180	(00 <sub>1</sub> )		
	63.349					(057)		
64.212	64.250			1.4493	48	(071)		
64.460	64.465			1.4443	58	(207)		
64.745	64.718			1.4387	326	(244)		
	64.792					(164)		
65.192	65.189			1.4299	140	(217)		
65.673	65.664			1.4206	142	(02 <sub>1</sub> )		
66.501	66.506			1.4049	461	(236)		
66.798	66.779			1.3994	221	(148)		
	66.841					(060)		
67.078	67.092			1.3942	239	(252)		
67.525	67.534			1.3860	323	(139)		
	67.543					(10 <sub>1</sub> )		
68.750	68.768			1.3643	120	(253)		
69.518	69.529			1.3511	140	(208)		
70.853	70.842			1.3289	67	(237)		
71.483	71.480			1.3187	146	(300)		
	71.490					(166)		
72.288	72.283	72.287		1.3060	461	(075)	( $\bar{2}$ 41)	
	72.302	72.326				(228)	(514)	
	72.331	72.331				(241)	(241)	
73.434	73.429			1.2884	543	(260)		
	73.470					(312)		
	74.014					(255)		
74.025	74.035			1.2796	698	(059)		
	74.043					(04 <sub>1</sub> )		
74.540	74.544			1.2720	150	(321)		

## Results

SrNb<sub>2</sub>O<sub>6</sub>. Unit cell parameters, cell content and figures of merit for the indexing are given in Table 1. The indexed pattern is shown in Table 2. Reflections with indices (*h0l*) were observed only for *l* = 2*n* and (*0k0*) only for *k* = 2*n*, which is characteristic of space group *P2<sub>1</sub>/c*. Trial parameters for atomic coordinates were derived from the orthorhombic modification of CaTa<sub>2</sub>O<sub>6</sub> reported by Jahnberg.<sup>9</sup> Full-profile Rietveld refinement was made by the program written by Werner *et al.*<sup>13</sup> The refinement was terminated when all shifts in the parameters were less than 10 % of their corresponding standard deviations. The final reliability factor *R<sub>F</sub>*, defined below, was 0.10.

$$R_F = \frac{\sum_{hkl} |\sqrt{I_{obs}} - \sqrt{I_{calc}}|}{\sum_{hkl} |\sqrt{I_{obs}}|}$$

The positional parameters obtained are given in Table 3. Because of the strong correlation between temperature and absorption effects, no thermal parameters of physical significance could be derived. Half-width, asymmetry and zero-point parameters were refined together with the atomic coordinates. The observed and calculated intensity curves are shown in Fig. 1. In order to facilitate a comparison between the curves, the scale is increased so that only 1/3 of the strongest diffraction peak at 2θ = 29° is shown in the figure.

The structure is built up from two crystallographically independent NbO<sub>6</sub> octahedra, sharing

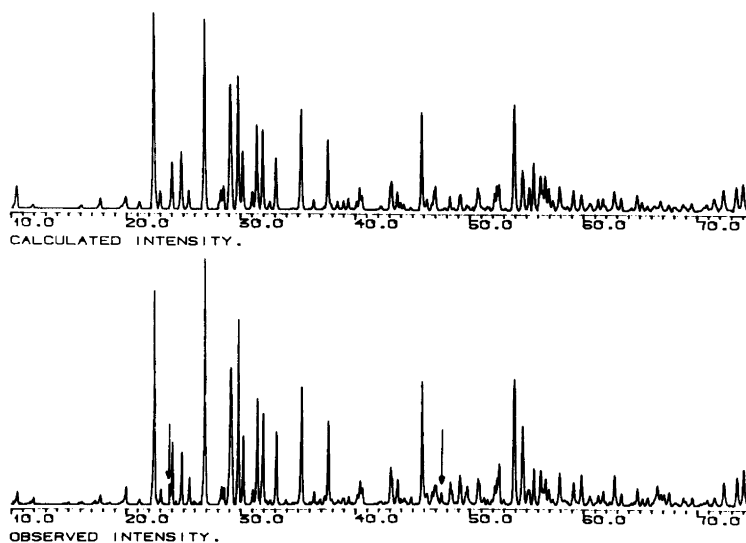


Fig. 3. Observed and calculated X-ray powder diffraction intensities for a mixed pattern of  $\text{SrNb}_6\text{O}_{16}$  and  $\text{SrNb}_2\text{O}_6$  in the molar ratio 5:1. Small contributions from  $\text{Nb}_2\text{O}_5$  are marked out by arrows at  $2\theta = 23.7^\circ$  and  $47.5^\circ$ .

edges and corners (Fig. 2 and Table 4). Two different pairs of octahedra with Nb-Nb distances 3.174(9) Å and 3.205(9) Å are formed by sharing edges. In the isostructural  $\text{CaTa}_2\text{O}_6$ , all  $\text{TaO}_6$  octahedra are identical. Nb(1), O(1) and O(3) form layers in the  $bc$  plane, i.e. with  $x$  coordinates around zero; whereas, Nb(2), O(2) and O(4) form similar layers at  $x$  around 0.5. The layers are connected via the corner oxygens O(5) and O(6). The main difference between the present structure and the orthorhombic  $\text{CaTa}_2\text{O}_6$ , however, is that the two layers are not related by exact mirror planes at  $x = 1/4$  and  $3/4$ . The strontium atoms are situated in tunnels running in the direction of the  $a$  axis. The strontium atoms are surrounded by eight oxygens at distances from 2.43 to 2.68 Å. The average Sr-O distance is 2.54 Å, whereas the corresponding Ca-O distance in  $\text{CaTa}_2\text{O}_6$  is 2.50 Å. Considering the ionic radii for  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ , 0.99 Å and 1.12 Å respectively, it seems likely that the monoclinic deviation of the  $\text{SrNb}_2\text{O}_6$  structure is caused by the limited space for the strontium ions in the tunnels.

$\text{SrNb}_6\text{O}_{16}$ . After omission of all lines that can be attributed to the monoclinic phases  $\text{SrNb}_2\text{O}_6$  and  $\text{Nb}_2\text{O}_5$  (B and C in Table 5), the remaining lines may be used to derive the orthorhombic cell dimensions reported in Table 1. Although the powder pattern is similar to that of  $\text{NaNb}_6\text{O}_{15}\text{F}$ , the occurrence of some weak reflections with  $k+l = 2n+1$  excludes the space group  $\text{Amm}2$ .

Therefore, Rietveld refinements of the heavy atom positions were made in space group  $\text{Pmm}2$  by means of the two-phase program written by Werner *et al.*<sup>13</sup> The atomic coordinates for strontium and niobium were derived from the sodium and niobium positions reported by Andersson for  $\text{NaNb}_6\text{O}_{15}\text{F}$ .<sup>7</sup> The coordinates for the monoclinic  $\text{SrNb}_2\text{O}_6$  were held fixed at the values given in Table 3, and only the relative amount of this

Table 6. Fractional atomic coordinates in space group  $\text{Amm}2$  for  $\text{SrNb}_6\text{O}_{16}$  used to calculate the intensity curve for the mixed powder diffraction pattern shown in Fig. 3.

Atom	Point position	$x/a$	$y/b$	$z/c$
Sr(1)	2(b)	1/2	0	0.4040
Nb(1)	2(a)	0	0	0
Nb(2)	2(a)	0	0	0.2142
Nb(3)	4(d)	0	0.3186	0.0620
Nb(4)	4(d)	0	0.3153	0.3154
O(1)	2(b)	1/2	0	0
O(2)	2(b)	1/2	0	0.226
O(3)	4(e)	1/2	0.324	0.050
O(4)	4(e)	1/2	0.323	0.307
O(5)	4(d)	0	0.119	0.105
O(6)	4(d)	0	0.133	0.311
O(7)	4(d)	0	0.305	0.447
O(8)	4(d)	0	0.351	0.178
O(9)	2(a)	0	1/2	0.356
O(10)	2(a)	0	0	0.519



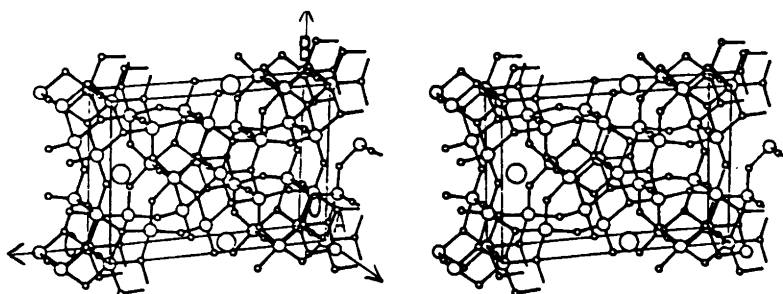


Fig. 4. Stereo view of SrNb<sub>6</sub>O<sub>16</sub>. Large circles = Sr, medium circles = Nb and small circles = O.

phase was refined. The small intensity contributions from Nb<sub>2</sub>O<sub>5</sub> were neglected since they could not appreciably affect the result. Because of the symmetry reduction from *Amm2* to *Pmm2*, the number of atomic positions increases from 15 to 30. By formal limitations in the computer program, however, it is not possible to refine more than 25 atomic positions in each phase. Although it may be possible to increase the program limits, it is judged as clearly unrealistic to include more than 25 atoms in a powder refinement, unless very strong constraints exist. Furthermore, although most of the oxygen atoms could be included in the intensity calculations, it was not possible to make any convergent refinement unless the oxygen positions were held fixed.  $R_F$  values in the range 0.17–0.20 were obtained from various refinements. No significant shifts in the input coordinates for strontium and niobium were found, however.

At this stage, it was decided to use space group *Amm2* and calculate the intensity curve and the  $R_F$  value from a Rietveld refinement with all atomic positions held fixed at the values reported by Andersson for NaNb<sub>6</sub>O<sub>15</sub>F.<sup>7</sup> The coordinates are listed in Table 6. In this refinement, only the relative amounts of the phases and nonstructural parameters such as half-width and asymmetry were refined. Considering the similarity between the observed and calculated intensity curves for the mixed pattern (Fig. 3), and the  $R_F$  value = 0.16 obtained, it can be concluded that the main contribution to the pattern is yielded by a phase that is isostructural with NaNb<sub>6</sub>O<sub>15</sub>F and that the deviations from space group *Amm2* are small. The composition of the phase should therefore be SrNb<sub>6</sub>O<sub>16</sub> (i.e. SrO · 3Nb<sub>2</sub>O<sub>5</sub>). It is also concluded that the reaction at 1000 °C between 2SrO · 5Nb<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> in the molar ratio 3:1 can be written: 3Sr<sub>2</sub>Nb<sub>10</sub>O<sub>27</sub> + Nb<sub>2</sub>O<sub>5</sub> → 5SrNb<sub>6</sub>O<sub>16</sub> + SrNb<sub>2</sub>O<sub>6</sub>.

The stoichiometry was confirmed by the refinement. In Fig. 4, a stereo view of the ideal structure in space group *Amm2* is given. As it was not found possible to use the correct space group, *Pmm2*, in the refinement of the structure, we can only speculate about the difference between the NaNb<sub>6</sub>O<sub>15</sub>F and the SrNb<sub>6</sub>O<sub>16</sub> structures. It seems likely, however, that the small deviations should be attributed to the increase in ionic radius from 0.95 Å for Na<sup>+</sup> to 1.12 Å for Sr<sup>2+</sup>.

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## References

1. Goldschmidt, H. J. *Metallurgia* 62 (1960) 211.
2. Francombe, M. H. *Acta Crystallogr.* 13 (1960) 131.
3. Whiston, C. D. and Smith, A. J. *Acta Crystallogr.* 23 (1967) 82.
4. Appendino, P. and Burlando, G. A. *Atti Accad. Sci. Torino* 107 (1973) 97.
5. Appendino, P. and Montorsi, M. *Chimica Industria* 57 (1975) 233.
6. Werner, P.-E., Eriksson, L. and Westdahl, M. J. *Appl. Crystallogr.* 18 (1985) 367.
7. Andersson, S. *Acta Chem. Scand.* 19 (1965) 2285.
8. Brusset, H., Gillier-Pandraud, H. and Voliotis, S. D. *Mat. Res. Bull.* 6 (1971) 5.
9. Jahnberg, L. *Acta Chem. Scand.* 71 (1963) 2548.
10. Deslattes, R. D. and Henins, A. *Phys. Rev. Lett.* 31 (1973) 972.
11. Hubbard, C. R., Swanson, H. E. and Mauer, F. A. *J. Appl. Crystallogr.* 8 (1975) 45.
12. Johansson, K. E., Palm, T. and Werner, P.-E. *J. Phys. E* 13 (1980) 1289.
13. Werner, P.-E., Salomé, S., Malmros, G. and Thomas, J. J. *Appl. Crystallogr.* 12 (1979) 107.
14. Trunov, V. K., Averina, I. M. and Velikodnij, J. A. *Kristallografiya* 26 (1980) 390.

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