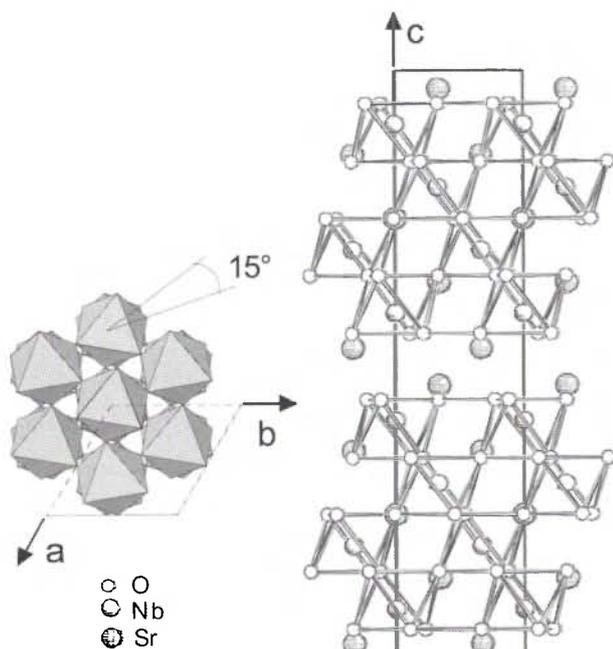


# Reinvestigation of the crystal structure of pentastrontium tetraniobate, $\text{Sr}_5\text{Nb}_4\text{O}_{15}$

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## Abstract

$\text{Nb}_4\text{O}_{15}\text{Sr}_5$ , trigonal,  $P\bar{3}c1$  (No. 165),  $a = 5.666(1)$  Å,  $c = 22.968(5)$  Å,  $V = 638.6$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_m = 5.48$  g·cm<sup>-3</sup>,  $R_{\text{gt}}(F) = 0.044$ ,  $wR(F^2) = 0.124$ ,  $T = 293$  K.

## Source of material

As  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$  decomposes peritectically at 1773 K, single crystals were obtained from a niobium-rich mixture (30% mol  $\text{Nb}_2\text{O}_5$  and 70% mol  $\text{SrCO}_3$ ) in a platinum crucible using the following thermal cycle: heating up to 1923 K at 10K/min, dwelling time 15h, then cooling down to 1673 K at 2K/h and finally cooling down to room temperature at 5K/h.

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Sr(1)	2a	0	0	1/4	0.0146(6)	$U_{11}$	0.0126(8)	$U_{11}/2$	0	0
Nb(2)	4d	1/3	2/3	0.30282(4)	0.0104(4)	$U_{11}$	0.0091(5)	$U_{11}/2$	0	0
Sr(3)	4d	1/3	2/3	0.14223(5)	0.0137(5)	$U_{11}$	0.0138(7)	$U_{11}/2$	0	0
Nb(1)	4c	0	0	0.09077(6)	0.0121(5)	$U_{11}$	0.0097(5)	$U_{11}/2$	0	0
Sr(5)	4d	1/3	2/3	0.46886(5)	0.0138(5)	$U_{11}$	0.0147(6)	$U_{11}/2$	0	0

## Discussion

The crystal structure of  $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ , achieved by Rietveld analysis of X-ray powder diffraction pattern using the structural parameters of  $\text{Ba}_5\text{Ta}_4\text{O}_{15}$  (trigonal symmetry, space group  $P\bar{3}m1$ ), results of a monoclinic distortion of the hexagonal cell [1]. However the refinement is quite poor: no  $R$  value, no thermal factors and no justification of choosing the monoclinic system were given. Moreover many atomic distances (mainly Nb—O and O—O) are anomalous with respect to the well-known crystal chemistry of niobates. The reinvestigation was done from single crystal X-ray diffraction data and preliminary electron diffraction analysis of the reciprocal lattice. It is definitively a member  $n = 5$  of the homologous series of complex oxides with cation-deficient perovskite-related structure with trigonal symmetry formulated as  $\text{A}_n\text{B}_{n-1}\text{O}_{3n}$ . The  $P\bar{3}c1$  space group chosen instead that of  $\text{Ba}_5\text{Ta}_4\text{O}_{15}$  [2, 3] corresponds to a doubling of the  $c$ -parameter due to a global reverse rotation of  $\text{TiO}_6$  octahedra ( $\sim 15^\circ$ ) around the  $c$  axis (see figure). As observed in  $\text{La}_5\text{Ti}_4\text{O}_{15}$  [4] and  $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$  [5], this cooperative rotation of all the octahedra is the simplest way to provide  $\text{Sr}^{2+}$  cations with a [6+3] coordination without any distortion of these octahedra. Due to the ionic radius of  $\text{Sr}^{2+}$ , such a coordination is better suited than the [12] coordination.

**Table 1.** Data collection and handling.

Crystal:	transparent, flat hexagonal prism, size $0.03 \times 0.12 \times 0.16$ mm
Wavelength:	Mo $K_\alpha$ radiation (0.71073 Å)
$\mu$ :	242.44 cm <sup>-1</sup>
Diffractometer, scan mode:	Siemens P4, $\omega$
$2\theta_{\text{max}}$ :	60.02°
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ :	1260, 559
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 331
$N(\text{param})_{\text{refined}}$ :	39
Programs:	SHELXL-97 [6], SCHAKAL [7]

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Table 2. Continued.

Atom	Site	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	12g	-0.3327(8)	-0.2230(8)	0.0557(2)	0.013(2)	0.015(2)	0.014(2)	0.006(2)	0.000(2)	-0.002(2)
O(2)	12g	0.6661(8)	-0.1252(9)	0.3465(2)	0.017(2)	0.021(2)	0.012(2)	0.008(2)	-0.001(2)	-0.005(2)
O(3)	6f	0	-0.5360(9)	1/4	0.020(3)	0.011(2)	$U_{11}$	$U_{11}/2$	-0.003(3)	-0.002(1)

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