

X-ray diffraction study of $K_3NdSi_7O_{17}$: a new framework silicate with a linear Si—O—Si bond**S. M. Haile^{a*} and B. J. Wuensch^b**^aMaterials Science, California Institute of Technology, Pasadena, CA 91125, USA, and^bDepartment of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

Correspondence e-mail: smhaile@caltech.edu

Received 20 December 1999

Accepted 3 May 2000

Hydrothermal investigations in the high-silica region of the $K_2O-Nd_2O_3-SiO_2$ system, carried out in a search for novel fast-ion conductors (FICs), yielded the new compound tripotassium neodymium heptasilicate, $K_3NdSi_7O_{17}$. Single-crystal X-ray methods revealed that $K_3NdSi_7O_{17}$ crystallizes in space group $P\bar{3}$, has lattice constants $a = 16.131(2)$ and $c = 7.7146(19)$ Å, $Z = 4$, and 22 atoms in the asymmetric unit. Refinement was carried out to a residual, $R(F)$, of 0.0253 and a weighted residual, $wR(F^2)$, of 0.0702 using anisotropic displacement parameters for all atoms. The silicate anion forms an interrupted framework, within which both Nd octahedra and K polyhedra are situated. The structure is unusual in that it contains a symmetry-constrained Si—O—Si bond angle of 180°. No isomorphs to $K_3NdSi_7O_{17}$ are known.

1. Introduction

As part of a broad effort to elucidate the relationship between alkali-ion transport and crystal structure we have carried out hydrothermal syntheses in the silica-rich region of the $K_2O-Nd_2O_3-SiO_2$ system (Haile *et al.*, 1993). Ion transport in silicate compounds has been of particular interest ever since fast-ion conductivity was reported in NASICON (Goodenough *et al.*, 1976) and also has relevance to geochemical systems. The present study was motivated, in particular, by a report on the structure of $K_3NdSi_6O_{15}$ (Pushcharovskii *et al.*, 1981). This silicate contains large one-dimensional channels that we anticipated would promote fast-ion transport. In the present work we report the structure of the compositionally similar compound, $K_3NdSi_7O_{17}$. As described below, the compact nature of the crystal structure in this latter silicate does not, in fact, lend itself to fast ion transport.

2. Experimental procedure and results**2.1. Synthesis**

Crystals of $K_3NdSi_7O_{17}$ were grown hydrothermally under isothermal conditions. In the hydrothermal technique high temperatures and pressures are employed to dissolve a normally insoluble precursor material and precipitate the stable crystalline phase; thus, the method is particularly well suited to inducing crystallization in silicates that otherwise form glasses when cooled from the melt (Laudise, 1987). The range of conditions that yielded the present compound have been described elsewhere (Haile *et al.*, 1993) and are briefly summarized as follows. The temperature and pressure were held at 773 K and 82.5 MPa, respectively; the precursor was a ground glass of composition $4 K_2O-Nd_2O_3-17SiO_2$ and the solvent 0.1–1 M KF or 0.1–0.25 M KHF₂ in distilled H₂O.

Table 1

Experimental details.

Crystal data	
Chemical formula	$\text{K}_3\text{NdO}_{17}\text{Si}_7$
Chemical formula weight	730.17
Cell setting	Hexagonal
Space group	$P\bar{3}$
a (Å)	16.131 (2)
b (Å)	16.131 (2)
c (Å)	7.175 (2)
V (Å ³)	1616.9 (5)
Z	4
D_x (Mg m ⁻³)	3.000
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	22
θ range (°)	23.6–33.3
μ (mm ⁻¹)	4.595
Temperature (K)	293 (2)
Crystal form	Irregular
Crystal color	Colorless
Data collection	
Diffractometer	Nonius four-circle
Data collection method	X-ray diffraction
Absorption correction	Psi scan
T_{\min}	0.277
T_{\max}	0.323
No. of measured reflections	2740
No. of independent reflections	2474
No. of observed reflections	2469
Criterion for observed reflections	$I \geq \sigma(I)$
R_{int}	0.0276
θ_{\max} (°)	27.50
Range of h, k, l	0 → h → 18 0 → k → 18 -9 → l → 9
No. of standard reflections	2
Intensity decay (%)	1.25
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0260
$wR(F^2)$	0.0702
S	1.277
No. of reflections used in refinement	2469
No. of parameters used	172
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 4.4536P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}$ (e Å ⁻³)	0.949
$\Delta\rho_{\min}$ (e Å ⁻³)	-1.717
Extinction method	<i>SHELXL93</i> (Sheldrick, 1993)
Extinction coefficient	0.0297 (7)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Data collection	Nonius Software
Cell refinement	Nonius Software
Data reduction	Nonius Software
Structure solution	<i>SHELXS86</i> (Sheldrick, 1985)
Structure refinement	<i>SHELXL93</i> (Sheldrick, 1993)

Experiments were allowed to proceed for a period of 8–13 d. Syntheses in which the KHF_2 concentration was greater than 0.25 M yielded the product $\text{K}_2\text{NdSi}_4\text{O}_{10}\text{OH}$, either as a second phase or as the sole product. Experiments in which the KF

concentration was greater than 1 M were not attempted. The presence of the fluoride ion was critical to the synthesis of $\text{K}_3\text{NdSi}_7\text{O}_{17}$ in that experiments utilizing pure water or up to 1 M of K_2CO_3 or KOH yielded the compound $\alpha\text{-K}_3\text{NdSi}_6\text{O}_{15}\cdot 2\text{H}_2\text{O}$ (Haile & Wuensch, 2000a).

In the vast majority of experiments $\text{K}_3\text{NdSi}_7\text{O}_{17}$ grew as relatively large crystals, up to 1 mm in length (along c) with a cross-sectional area of ~ 0.15 mm². The {100}, {011} and {001} forms were typically displayed. Crystals were generally of high optical quality and the synthesis experiments were highly reproducible.

2.2. Composition determination and thermal analysis

The chemical composition of $\text{K}_3\text{NdSi}_7\text{O}_{17}$ was determined from electron probe microanalyses of samples that had been previously confirmed to be of the desired phase through single-crystal X-ray diffraction. Both energy-dispersive X-ray analysis (EDX) and wavelength dispersive analysis (WDX) were performed, and the procedural details are described elsewhere (Haile *et al.*, 1993). The EDX measurements yielded normalized weight percentages of K_2O , Nd_2O_3 and SiO_2 of 20.0 (2), 22.8 (2) and 57.2 (1), respectively, which compare rather well with the ideal weight percentages of 19.3, 23.1 and 57.6 for $\text{K}_3\text{NdSi}_7\text{O}_{17}$. The WDX experiments yielded absolute mole percentages of K, Nd and Si of 10.65 (12), 3.41 (3) and 25.87 (25), respectively. Again, the values are quite comparable to those expected for a crystal of ideal composition, $\text{K}_3\text{NdSi}_7\text{O}_{17}$, of 10.7, 3.6 and 25.0 mol.%, respectively. Conversion of the mole percentages of metals to weight percentages of the respective oxides provides a sum of 101.3 (5) wt%, which is in good agreement with the expected value of 100%.

Differential scanning calorimetry was carried out on a ground powder sample at a heating rate of 20 K min⁻¹ using a Seiko DSC-320. No phase transitions were detected between room temperature and 1173 K.

2.3. Structure determination

X-ray intensity data were collected with a Nonius diffractometer using Mo $K\alpha$ radiation. Full details of the data collection parameters are given in Table 1. The positions of the cations Nd, K and Si were found by direct methods and those of the O atoms from subsequent difference Fourier maps. In the final cycle of the refinement anisotropic displacement parameters were refined for all 22 atoms in the asymmetric unit of $\text{K}_3\text{NdSi}_7\text{O}_{17}$ and a weighted residual, $wR(F^2) > -\sigma(F^2)$, of 0.0702 was obtained, Table 1. Direct methods calculations, structure factor calculations and least-squares refinements were carried out using the *SHELX* package of programs (Sheldrick, 1985, 1993).¹

The atomic coordinates and thermal displacement parameters for the 22 atoms in the asymmetric unit of $\text{K}_3\text{NdSi}_7\text{O}_{17}$

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS0011). Services for accessing these data are described at the back of the journal.

Table 2

Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for $\text{K}_3\text{NdSi}_7\text{O}_{17}$.

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	Position	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Nd(1)	1 <i>a</i> $\bar{3}$.	0	0	0	0.926 (12)
Nd(2)	3 <i>e</i> $\bar{1}$.	-1/2	-1/2	0	0.952 (11)
Si(1)	2 <i>d</i> $\bar{3}$.	2/3	1/3	0.4247 (2)	0.96 (3)
Si(2)	6 <i>g</i> 1	-0.71320 (6)	-0.61966 (6)	-0.69845 (12)	0.92 (2)
Si(3)	6 <i>g</i> 1	-0.69315 (6)	-0.52568 (6)	-0.32686 (12)	0.94 (2)
Si(4)	2 <i>d</i> $\bar{3}$.	2/3	1/3	0.8654 (2)	0.95 (3)
Si(5)	6 <i>g</i> 1	-0.84320 (6)	-0.83555 (6)	0.37820 (12)	0.91 (2)
Si(6)	6 <i>g</i> 1	-0.46020 (6)	-0.25155 (6)	-0.97903 (12)	0.96 (2)
K(1)	6 <i>g</i> 1	-0.53819 (6)	-0.63419 (7)	-0.46846 (11)	2.48 (2)
K(2)	6 <i>g</i> 1	-0.76102 (7)	-0.75708 (7)	-0.12460 (14)	3.00 (2)
O(1) _{br}	6 <i>g</i> 1	-0.7815 (2)	-0.6254 (2)	-0.8735 (3)	1.38(5)
O(2) _{br}	6 <i>g</i> 1	-0.8184 (2)	-0.8893 (2)	-0.4567 (3)	1.49 (5)
O(3) _{br}	6 <i>g</i> 1	-0.7477 (2)	-0.7296 (2)	-0.6374 (3)	1.46 (5)
O(4) _{br}	6 <i>g</i> 1	-0.7720 (2)	-0.3628 (2)	-0.3536 (4)	1.65 (5)
O(5) _{br}	6 <i>g</i> 1	-0.7888 (2)	-0.5590 (2)	-0.2006 (3)	1.40 (5)
O(6) _t	6 <i>g</i> 1	-0.9802 (2)	-0.8692 (2)	-0.1837 (3)	1.64 (5)
O(7) _t	6 <i>g</i> 1	-0.6217 (2)	-0.5550 (2)	-0.2425 (3)	1.67 (5)
O(8) _t	6 <i>g</i> 1	-0.4585 (2)	-0.3436 (2)	-0.9172 (4)	1.86 (5)
O(9) _{br}	6 <i>g</i> 1	-0.7409 (2)	-0.5710 (2)	-0.5283 (3)	1.57 (5)
O(10) _t	6 <i>g</i> 1	-0.3971 (2)	-0.4366 (2)	-0.2560 (3)	1.57 (5)
O(11) _{br}	6 <i>g</i> 1	-0.5614 (2)	-0.2550 (2)	-0.9349 (4)	1.79 (5)
O(12) _{br}	2 <i>d</i> $\bar{3}$.	1/3	2/3	0.3548 (6)	3.45 (13)

are given in Tables 2 and 3, respectively. Selected interatomic distances and angles in the cation coordination polyhedra of $\text{K}_3\text{NdSi}_7\text{O}_{17}$ are provided in Tables 4 and 5. Oxygen atoms are given the subscript t to indicate that they are terminating with respect to the silicate anion, *i.e.* are bonded to only one Si atom, and are given the subscript br to indicate that they are bridging with respect to silicate anions, *i.e.* are bonded to two Si atoms. The sum of the bond valences at each atomic position is provided in Table 6. The valences of the Si–O, Nd–O and K–O bonds were calculated according to

$$S(\text{Si}-\text{O}) = \exp[(1.624 - d_{\text{Si}-\text{O}})/0.37] \quad (1)$$

$$S(\text{Nd}-\text{O}) = \exp[(2.105 - d_{\text{Nd}-\text{O}})/0.37] \quad (2)$$

$$S(\text{K}-\text{O}) = \exp[(2.132 - d_{\text{K}-\text{O}})/0.37] \quad (3)$$

after Brown & Altermatt (1985), where $d_{\text{Si}-\text{O}}$, $d_{\text{Nd}-\text{O}}$ and $d_{\text{K}-\text{O}}$ are the respective bond lengths measured in \AA .

3. Discussion of the structure

The structure of $\text{K}_3\text{NdSi}_7\text{O}_{17}$ is shown in projection along [001] in Fig. 1. The compound contains a framework silicate anion of stoichiometry $[\text{Si}_7\text{O}_{17}]_n$. As the Si:O ratio in the stoichiometry suggests, there is an average of 3.14 bridging and 0.86 terminating O atoms per silicate tetrahedra. Specifically, one of seven silicate groups per formula unit contains entirely bridging O atoms, whereas the remaining six contain one terminating and three bridging O atoms. Such framework silicates, in which terminating O atoms exist within a structure

Table 3

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for $\text{K}_3\text{NdSi}_7\text{O}_{17}$.

The anisotropic displacement factors are of the form: $\exp\{-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]\}$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nd(1)	0.967 (14)	0.967 (14)	0.85 (2)	0	0	0.483 (7)
Nd(2)	0.946 (14)	0.860 (14)	0.88 (2)	0.065 (7)	0.054 (7)	0.325 (9)
Si(1)	1.04 (4)	1.04 (4)	0.81 (6)	0	0	0.52 (2)
Si(2)	0.90 (4)	0.94 (4)	0.84 (4)	0.05 (3)	0.06 (3)	0.40 (3)
Si(3)	0.98 (4)	1.05 (4)	0.93 (4)	0.05 (3)	-0.02 (3)	0.61 (3)
Si(4)	1.02 (4)	1.02 (4)	0.80 (6)	0	0	0.51 (2)
Si(5)	0.91 (4)	0.90 (4)	0.95 (4)	0.01 (3)	0.01 (3)	0.48 (3)
Si(6)	1.11 (4)	0.87 (4)	0.95 (4)	0.08 (3)	0.06 (3)	0.55 (3)
K(1)	3.09 (4)	3.51 (5)	2.04 (4)	0.46 (3)	0.47 (3)	2.56 (4)
K(2)	3.13 (5)	2.66 (4)	3.11 (5)	-0.36 (3)	0.29 (4)	1.38 (4)
O(1) _{br}	1.70 (11)	1.12 (11)	1.23 (11)	-0.10 (8)	-0.38 (9)	0.63 (9)
O(2) _{br}	1.81 (12)	1.10 (11)	1.68 (11)	0.13 (9)	-0.20 (9)	0.81 (9)
O(3) _{br}	1.16 (11)	0.86 (10)	2.21 (12)	0.37 (9)	-0.03 (9)	0.39 (9)
O(4) _{br}	1.16 (11)	1.22 (11)	2.65 (13)	-0.11 (9)	0.13 (9)	0.65 (9)
O(5) _{br}	1.24 (11)	1.89 (12)	1.01 (10)	0.02 (9)	0.06 (8)	0.73 (9)
O(6) _t	1.98 (12)	1.58 (11)	1.27 (11)	0.09 (9)	-0.30 (9)	0.83 (10)
O(7) _t	1.73 (12)	1.98 (12)	1.84 (12)	-0.15 (9)	-0.40 (9)	1.33 (10)
O(8) _t	2.89 (14)	1.30 (11)	1.81 (12)	0.22 (9)	-0.11 (10)	1.36 (11)
O(9) _{br}	1.68 (11)	2.30 (12)	1.03 (11)	-0.32 (9)	-0.08 (9)	1.22 (10)
O(10) _t	1.06 (11)	1.68 (11)	1.68 (12)	0.55 (9)	0.36 (9)	0.47 (9)
O(11) _{br}	1.05 (11)	1.29 (11)	2.78 (14)	-0.08 (10)	0.37 (10)	0.40 (9)
O(12) _{br}	4.8 (2)	4.8 (2)	0.7 (2)	0	0	2.42 (10)

comprised primarily of bridging O atoms, are sometimes classified as ‘interrupted’ framework structures, to distinguish them from silicates in which all O atoms are bridging. The average Si–O_{br} bond length in $\text{K}_3\text{NdSi}_7\text{O}_{17}$ is 1.629 \AA and the average Si–O_t is 1.573 \AA . The shortening of the Si–O_t bond lengths compared with the Si–O_{br} bond lengths (by an average of 0.056 \AA) results from the stronger attraction between O and Si than between O and the other cations in the structure, and is a typical result for silicates. The somewhat unusual Si–O(12)_t bond lengths are discussed below, in the

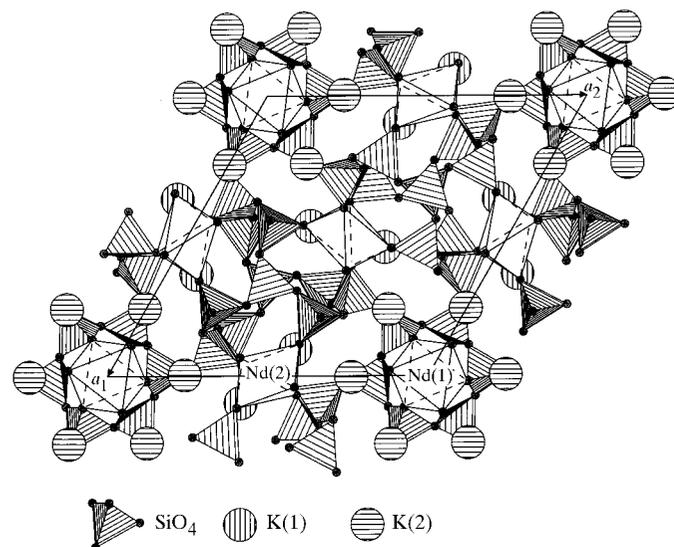


Figure 1

Projection of the structure of $\text{K}_3\text{NdSi}_7\text{O}_{17}$ along [001], showing NdO_6 and SiO_4 polyhedra.

Table 4

Interatomic distances and bond angles in the neodymium and silicon coordination polyhedra in $K_3NdSi_7O_{17}$.

The numbers in parentheses after a refined distance or angle indicates the standard uncertainty in the last digit(s). For averages, the number in parentheses indicates the standard deviation between individual values.

	Bond distance (Å)		Oxygen separation along edge (Å)		O—M—O angle (°)
Nd(1)	O(6) _t 6×	2.371 (2)	O(6)—O(6') 6×	3.291 (4)	87.92 (8)
			O(6)—O(6'') 6×	3.423 (4)	92.08 (8)
	Average	2.371		3.357 (66)	
Nd(2)	O(10) _t 2×	2.340 (2)	O(10)—O(8) 2×	3.260 (4)	88.29 (9)
	O(8) _t 2×	2.340 (2)	O(10)—O(8) 2×	3.359 (4)	91.71 (9)
	O(7) _t 2×	2.435 (2)	O(10)—O(7) 2×	3.141 (3)	82.23 (9)
			O(10)—O(7) 2×	3.598 (4)	97.77 (9)
			O(8)—O(7) 2×	2.790 (4)	71.48 (8)
		O(8)—O(7) 2×	3.876 (4)	108.52 (8)	
	Average	2.372 (42)		3.34 (27)	
Si(1)	O(12) _{br}	1.583 (5)	O(4)—O(12) 3×	2.585 (4)	108.56 (11)
	O(4) _{br} 3×	1.601 (2)	O(4)—O(4') 3×	2.629 (4)	110.35 (10)
Si(2)	O(10) _t	1.576 (2)	O(10)—O(9)	2.663 (3)	112.36 (13)
	O(9) _{br}	1.630 (2)	O(10)—O(3)	2.640 (3)	110.83 (13)
	O(3) _{br}	1.631 (2)	O(10)—O(1)	2.698 (3)	113.97 (13)
	O(1) _{br}	1.642 (2)	O(9)—O(3)	2.625 (3)	107.21 (13)
			O(9)—O(1)	2.599 (3)	105.20 (13)
Si(3)	O(7) _t	1.569 (2)	O(3)—O(1)	2.628 (3)	106.83 (12)
	O(9) _{br}	1.629 (2)	O(7)—O(9)	2.733 (3)	117.44 (13)
	O(5) _{br}	1.631 (2)	O(7)—O(5)	2.680 (3)	113.75 (13)
	O(4) _{br}	1.639 (3)	O(7)—O(4)	2.611 (3)	108.92 (14)
			O(9)—O(5)	2.512 (3)	100.82 (12)
Si(4)	O(12) _{br}	1.579 (5)	O(9)—O(4)	2.611 (4)	106.03 (14)
	O(11) _{br} 3×	1.608 (2)	O(5)—O(4)	2.668 (3)	109.32 (13)
	O(6) _t	1.582 (2)	O(11)—O(12) 3×	2.579 (5)	108.07 (11)
	O(2) _{br}	1.632 (2)	O(11)—O(11') 3×	2.647 (3)	110.85 (10)
	O(3) _{br}	1.635 (2)	O(6)—O(2)	2.677 (3)	112.23 (13)
Si(5)	O(2') _{br}	1.642 (2)	O(6)—O(3)	2.656 (3)	111.30 (13)
			O(6)—O(2')	2.707 (3)	114.78 (13)
			O(2)—O(3)	2.585 (3)	104.61 (13)
			O(2)—O(2')	2.632 (3)	107.00 (11)
			O(3)—O(2')	2.622 (3)	106.28 (13)
Si(6)	O(8) _t	1.563 (2)	O(8)—O(5)	2.658 (3)	113.01 (13)
	O(5) _{br}	1.624 (2)	O(8)—O(11)	2.681 (4)	113.82 (14)
	O(11) _{br}	1.636 (3)	O(8)—O(1)	2.643 (3)	110.65 (14)
	O(1) _{br}	1.651 (2)	O(5)—O(11)	2.605 (3)	106.04 (13)
			O(5)—O(1)	2.606 (3)	105.49 (13)
		O(11)—O(1)	2.647 (3)	107.30 (13)	

(Si—O_t) = 1.573 (6), (Si—O_{br}) = 1.629 (11), (O—O) = 2.637 (35) Å; (O—Si—O) = 109.4 (31)°.

Table 5

Interatomic distances in the potassium coordination polyhedra in $K_3NdSi_7O_{17}$.

Distances to next-nearest oxygen neighbors are given below the dotted line. The numbers in parentheses after a distance indicates the standard deviation in the last digit. Only oxygen distances less than the distance to the closest cation are reported.

K(1) neighbor	Distance (Å)	K(2) neighbor	Distance (Å)
O(10) _t	2.738 (3)	O(1) _{br}	2.927 (3)
O(8) _t	2.787 (3)	O(6) _t	2.958 (3)
O(7) _t	2.793 (3)	O(7) _t	3.011 (3)
O(4) _{br}	2.854 (3)	O(2) _{br}	3.018 (3)
O(9) _{br}	2.932 (3)	O(8) _t	3.085 (3)
O(5) _{br}	3.135 (2)	O(6) _t	3.092 (3)
O(3) _{br}	3.172 (2)	O(1) _{br}	3.133 (3)
O(10) _{br}	3.226 (3)	O(5) _{br}	3.484 (3)
O(7) _t	3.520 (3)	O(3) _{br}	3.517 (3)

context of the Si—O(12)—Si bond geometry. The values of the O—O separations within the SiO₄ tetrahedra range from 2.512

to 2.698 Å and have an average value of 2.637 Å. The O—Si—O bond angles range from 100.8 to 117.4°. These are, again, rather typical of silicate structures (Liebau, 1985).

Both the Nd(1) and Nd(2) atoms in $K_3NdSi_7O_{17}$ are coordinated by six O atoms. The overall stoichiometry implies that there are six terminating O atoms per formula unit, which, in turn, suggests that the NdO₆ octahedra should be formed entirely of such O atoms. Examination of Table 4 indeed reveals this to be the case. Nd(1) is coordinated by six O(6) atoms, which are terminating with respect to the Si(5)O₄ tetrahedron, whereas Nd(2) is coordinated by O(10), O(8) and O(7), which are terminating with respect to Si(2), Si(6) and Si(3), respectively. The sum of the bond valences at these terminating O-atom positions is lower than that at the bridging O-atom positions, in analogy to the results found earlier for Na₃NdSi₆O₁₅·2H₂O (Haile *et al.*, 1995). The Nd(1)O₆ polyhedron is centered at a site of $\bar{3}$ symmetry and is rather regular. The O—Nd—O angles differ from 90° by only ~2°. In contrast, the Nd(2)O₆ octahedron is highly distorted, with interpolyhedral angles ranging from 71.5 to 108.5°. Despite these differences, the sums of the bond valences at both Nd(1) and Nd(2) are quite close to 3, Table 6.

Turning to the configuration of the silicate anion in $K_3NdSi_7O_{17}$, the [Si₇O₁₇]_n framework can be understood in terms of two types of structural units. The first is a rather unusual 'three-sided ladder', which extends in a direction parallel to *c* and is centered at the threefold rotation axis at 2/3, 1/3, *z*. This unit is shown in projection on the (320) plane in Fig. 2. For clarity, only Si atoms and the connections between them are depicted. Triplets of five-membered rings [Si(4)—Si(6)—Si(2)—Si(3)—Si(1)] alternate with loosely defined eight-membered groups to form the ladder configuration. The second structural unit is a more conventional six-membered ring, comprised entirely of Si(5) tetrahedra and centered over the threefold rotation axis at 0, 0, *z* (not shown in Fig. 2). The ladder units and six-membered rings are connected *via* Si(2)—Si(5) linkages at ~0.65 in *c* to form an overall three-dimensional structure. The Nd(1)O₆ octahedra lie directly above and below the silicate six-membered rings, whereas the Nd(2)O₆ octahedra serve to link neighboring ladder units. Both of these relationships are evident in Fig. 3, a skeletal depiction of the structure in which only Si and Nd

Table 6
Bond strengths (bond valence units) and summation of bond strengths for the ions in $K_3NdSi_7O_{17}$.

See text for definition of formulae used for calculating individual bond valences.

Anion	Nd(1)	Nd(2)	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	K(1)	K(2)	Sum
O(1)				0.95				0.93		0.11	2.06
O(1')										0.07	
O(2)							0.98			0.09	2.02
O(2')							0.95				
O(3)				0.98			0.97		0.06		2.01
O(4)			1.06†		0.96				0.14		2.16
O(5)					0.98			1.00	0.06		2.05
O(6)	0.49						1.12			0.10	1.79
O(6')										0.07	
O(7)		0.39			1.16				0.16	0.09	1.80
O(8)		0.53						1.18	0.17	0.07	1.95
O(9)				0.98	0.99				0.11		2.08
O(10)		0.53		1.14					0.19		1.91
O(10')									0.05		
O(11)						1.04†		0.97			2.01
O(12)			1.12			1.13					2.25
Sum	2.92	2.90	4.31	4.06	4.09	4.26	4.02	4.08	0.94	0.61	

† Multiplicity of 3 with respect to bond-valence sum at the cation.

atoms are shown. The NdO_6 polyhedra are arranged within the silicate framework in a simple hexagonal array with effective lattice constants of $a_{Nd} = a/2 = 8.07$ and $c_{Nd} = c = 7.17$ Å. This placement of Nd atoms is reminiscent of the structures of $AM_xSi_6O_{15}$ layered silicates, in which the M^{3+} or M^{4+} cations take on an almost simple cubic array, with an effective lattice constant of ~ 7.5 Å (Haile & Wuensch, 1997, 2000b).

The most remarkable feature of the structure of $K_3NdSi_7O_{17}$ is the geometry about the Si(1)–O(12)–Si(4) bond. Examination of Fig. 2 and Table 2 reveals that these three atoms are colinear, each residing directly on the three-fold axis at $2/3, 1/3, z$. Accordingly, the Si(1)–O(12)–Si(4)

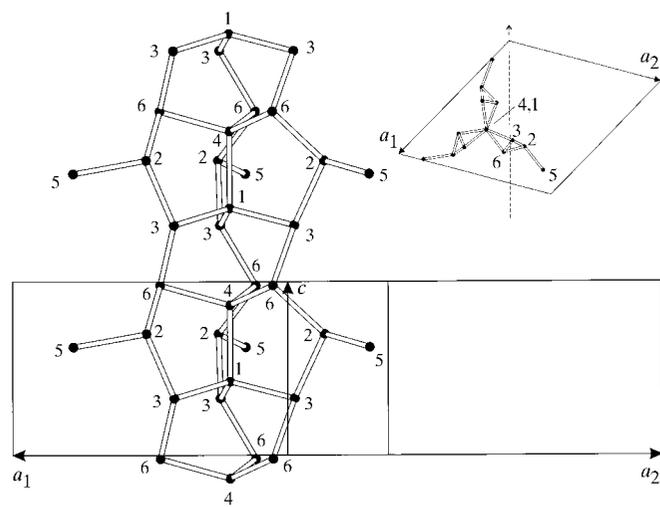


Figure 2
Connectivity between Si atoms in the ladder-like configuration in $K_3NdSi_7O_{17}$. Numbers indicate the identity of the Si atom. The structural unit is shown in projection on the (320) plane. The inset clarifies the viewing direction.

angle is linear. Moreover, O(12) is one of only two bridging atoms out of a total of eight which are bonded only to the two Si atoms it bridges, and not to K atoms. This is consistent with the general observation that the Si–O–Si angle increases as the oxygen coordination number decreases from three to two (Gibbs, 1982). From an evaluation of the structures of several hundred silicates conducted by Baur (1980), Liebau has concluded that an unstrained Si–O–Si bond will take on an angle of $\sim 139^\circ$ and that truly linear bonds are energetically unfavorable (Liebau, 1985). Liebau has further argued that crystallographically determined values of 180° are more likely to represent a time average rather than the actual value of the bond angle. The bond, at any instant in time, should have an O

atom displaced from its average position such that the instantaneous value of Si–O–Si is less than 180° . Similarly, one can argue that the true, instantaneous values of the Si–O bond lengths are greater than their apparent (average) values. Such an effect (*i.e.* large difference between instantaneous and average O-atom coordinates) should be detectable in the form of unusually large thermal-displacement parameters for the O atom in the Si–O–Si bond. This is indeed the case for O(12). The displacement parameters for this atom are about twice those of the other O atoms in the structure, with the greatest thermal displacement occurring in the plane perpendicular to the Si(1)–O(12)–Si(4) vector, Fig. 4. This difference between instantaneous and average structure is also likely to be responsible for the apparent overbonding at O(12), Table 6.

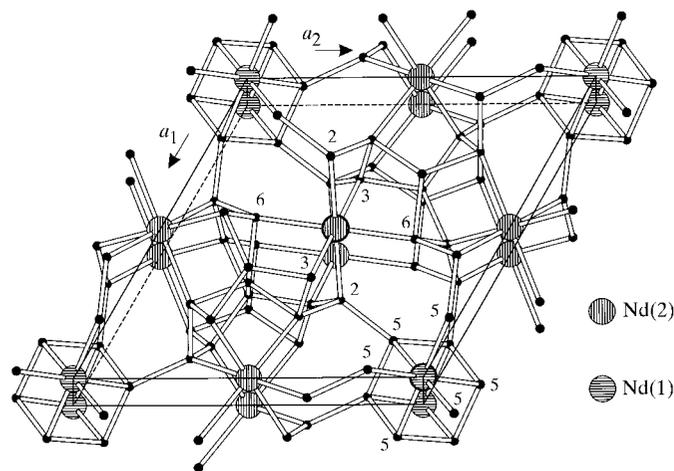


Figure 3
Overall connectivity between Si and Nd atoms in the structure of $K_3NdSi_7O_{17}$. The structure is viewed along a direction close to [001]. Si atoms which are linked to highlighted Nd atoms are as labeled.

That is, if the O(12) atom precesses about the Si(1)··Si(4) vector and $d_{\text{Si-O}}^{\text{inst}} > d_{\text{Si-O}}^{\text{ave}}$, the bond valences due to the Si(1)–O(12) and Si(4)–O(12) bonds should be less than calculated. It must be noted, however, that in order to obtain typical Si–O_{br} bond lengths of 1.63 Å, an Si–O–Si bond angle of 152°, and a bond-valence sum at O(12) of ~2, the mean displacement of the O atom must be 0.4 Å, a value which cannot be justified solely by the thermal displacement parameters of this atom (Table 3). Furthermore, refinements in which the O(12) was displaced from the threefold axis (and distributed over three neighboring sites) yielded an even shorter Si–O bond distance. Thus, the Si(1)–O(12) bond must, to some extent, be truly strained.

The remaining atoms of the structure, the two crystallographically distinct potassium ions, are located within the interstices of the NdSi₇O₁₇ framework in an alternating fashion, such that the K(1) atoms reside within the plane defined by $z \simeq 0.5$ and the K(2) atoms within the plane defined by $z \simeq 0$. The K(2) atoms are coordinated by seven O atoms and each K(2)O₇ polyhedra shares two O(1)–O(6) edges to form a six-membered ring, Fig. 5(a). The K(1) atoms, in contrast, are coordinated by eight O atoms and their polyhedra are linked pairwise *via* the O(10)–O(10) edge. Alternatively, if one includes a second O(7) atom, located at a distance of 3.52 Å from the cation, as a corner of the K(1) polyhedron, neighboring K(1)O₉ appear to share an O(10)–O(7)–O(10)–O(7) face. Both of these possible interpretations of the linkage are evident in Fig. 5(b). The K(1) and K(2) polyhedra are, in turn, linked to one another *via* the shared O(7)–O(8) edge. Overall, both terminating and bridging O atoms (with respect to Si) coordinate the K atoms. The large deviation of the bond sum at the K-atom sites from the expected value of 1, particularly K(2), is rather typical of large alkali ions with shallow bond-energy curves.

The conductivity of K₃NdSi₇O₁₇ has been measured and is reported elsewhere (Haile *et al.*, 1992). Both σ_{11} and σ_{33} are quite small, approximately $6 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 873 K. The mode of linkage between potassium-ion sites (primarily edge-

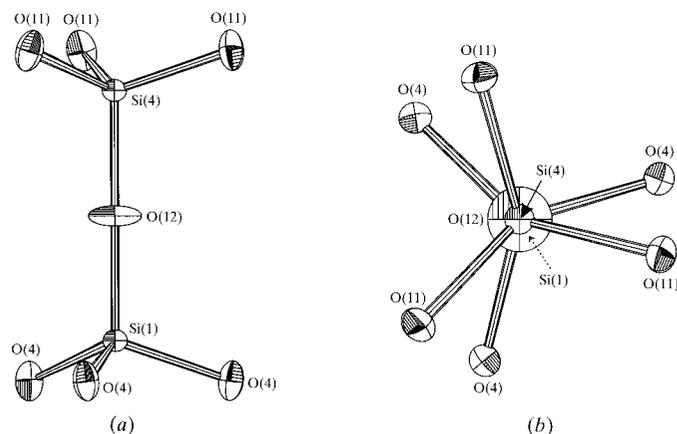


Figure 4

Thermal ellipsoid representation of the Si(1)O₃–O–Si(4)O₃ group in K₃NdSi₇O₁₇ located at 2/3, 1/3, z , shown in projection along (a) [210] and (b) [001].

shared polyhedra as opposed to face-shared) and the relatively low thermal displacement parameters of K(1) and K(2) in K₃NdSi₇O₁₇ are consistent with this observation of low ionic conductivity. Moreover, the structure is quite compact, with a density of 3.00 g cm⁻³ compared with 2.68 g cm⁻³ for α -K₃NdSi₆O₁₅·H₂O (Haile & Wuensch, 2000a), another factor leading to low ionic conductivity.

The authors are grateful to Karl Peters of the Max-Planck-Institut für Festkörperforschung for collecting single-crystal intensity data and aiding with the structure determination. Steve Recca and Mike Jercinovic of the Massachusetts Institute of Technology kindly carried out microprobe analyses. SMH thanks Joachim Maier for hosting her visit to MPI where some portions of this research were carried out. This work is dedicated to the memory of the late Robert A. Laudise, in whose laboratory the hydrothermal syntheses were carried out.

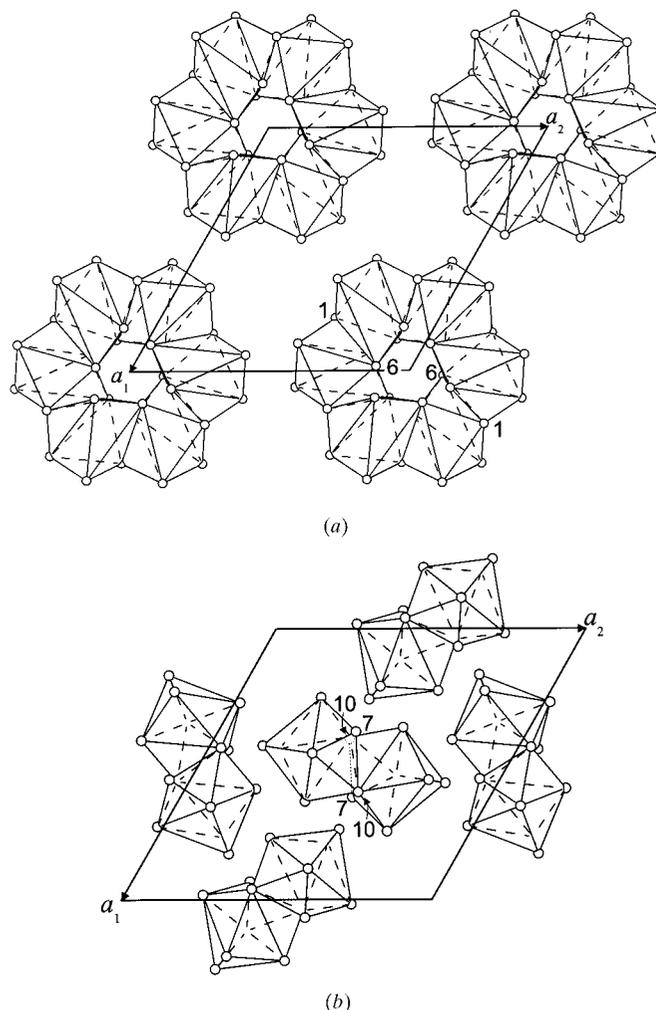


Figure 5

Projections of the structure of K₃NdSi₇O₁₇ along [001] showing the coordination polyhedra about potassium ions. O atoms involved in forming shared polyhedral edges or faces are labeled. (a) Projection from $z = -0.5$ to $z = 0.5$, showing polyhedra about K(2); (b) projection from $z = 0.1$ to $z = 0.9$, showing polyhedra about K(1). Si and Nd atoms, and those O atoms not bonded to K, have been omitted for clarity.

References

- Baur, W. H. (1980). *Acta Cryst.* **B36**, 2198–2202.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Gibbs, G. V. (1982). *Am. Mineral.* **67**, 421–450.
- Goodenough, J. B., Hong, H. Y. P. & Kafalas, J. A. (1976). *Mater. Res. Bull.* **11**, 203–220.
- Haile, S. M., Maier, J., Wuensch, B. J. & Laudise, R. A. (1995). *Acta Cryst.* **B51**, 673–680.
- Haile, S. M. & Wuensch, B. J. (1997). *Am. Mineral.* **82**, 1141–1149.
- Haile, S. M. & Wuensch, B. J. (2000a). *Acta Cryst.* **B56**, 335–348.
- Haile, S. M. & Wuensch, B. J. (2000b). *Acta Cryst.* **B56**, 349–362.
- Haile, S. M., Wuensch, B. J., Laudise, R. A., Opila, R., Siegrist, T. & Foxman, B. M. (1993). *The Structural Chemistry of Silicates*, pp. 77–94. Buffalo, NY: Trans. Am. Cryst. Assoc., American Crystallographic Association.
- Haile, S. M., Wuensch, B. J., Siegrist, T. & Laudise, R. A. (1992). *Solid State Ion.* **53–56**, 1292–1301.
- Haile, S. M., Wuensch, B. J., Siegrist, T. & Laudise, R. A. (1993). *J. Cryst. Growth*, **131**, 352–372.
- Laudise, R. A. (1987). In *Advanced Crystal Growth*, edited by P. M. Dryburgh, B. Cockayne and K. G. Barrachlough, pp. 267–286. New York: Prentice Hall.
- Liebau, F. (1985). *Structural Chemistry of Silicates: Structure, Bonding, and Classification*, pp. 14–29. Berlin: Springer-Verlag.
- Pushcharovskii, D. Y., Dago, A. M., Podeminskaya, E. A. & Belov, N. V. (1981). *Sov. Phys. Dokl.* **26**, 552–554 (in english).
- Sheldrick, G. M. (1985). *Crystallographic Computing*, edited by G. M. Sheldrick, C. Krüger and R. Goddard, Vol. 3, pp. 175–189. New York: Oxford University Press.
- Sheldrick, G. M. (1993). *Crystallographic Computing*, edited by H. D. Flack, L. Parkanyi and K. Simon, pp. 100–110. New York: Oxford University Press.