

# Lithium and sodium yttrium orthosilicate oxyapatite, $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ and $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ , at both 100 K and near room temperature

Günther R. Redhammer\* and G. Roth

Institute of Crystallography, RWTH–Aachen, Jägerstraße 17/19, D-52056 Aachen, Germany

Correspondence e-mail: guenther.redhammer@aon.at

Received 10 October 2003

Accepted 15 October 2003

Online 8 November 2003

Lithium yttrium orthosilicate oxyapatite [lithium nonayttrium hexakis(silicate) dioxide],  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ , crystallizes in the centrosymmetric space group  $P6_3/m$  at both 295 and 100 K. The structure closely resembles those of fluorine apatite and sodium yttrium orthosilicate oxyapatite [sodium nonayttrium hexakis(silicate) dioxide],  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ , which was also investigated, at 270 and 100 K, in this study. There are two different crystallographic sites for the  $\text{Y}^{3+}$  ion, which are coordinated by seven and nine O atoms. One-fourth of the nine-coordinated site is occupied by Li or Na atoms, thus maintaining charge balance. The Si atom occupies a tetrahedral site. The two compounds show no symmetry change between room temperature and 100 K, and the alterations in structural parameters are small.

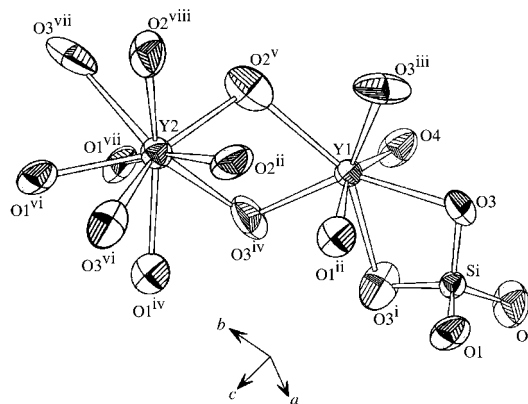
## Comment

Apatite-type compounds [general formula  $M_{10}(\text{XO}_4)_6\text{Z}_2$ ] show a wide range of chemical variety and occur as both natural and synthetic compounds, with high relevance in industrial and biological research (White & ZhiLi, 2003). In natural apatite, the Z site is usually occupied by F, Cl or OH atoms, but in oxyapatite, O atoms also occur in this site. The title compounds can be derived from  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  (apatite *sensu stricto*) by replacing the  $\text{Ca}^{2+}$  ions with  $\text{Y}^{3+}$  ions (or other trivalent cations, such as rare earth elements), the  $\text{PO}_4^{3-}$  ions with  $\text{SiO}_4^{4-}$  ions and the  $\text{F}^-$  ions with  $\text{O}^{2-}$  ions. Charge balance is maintained in various ways in such orthosilicate oxyapatites. If trivalent cations are assumed, the M site may contain cation defects (cation vacancies), as is the case in  $\text{Gd}_{9.33}\square_{0.67}(\text{SiO}_4)_6\text{O}_2$  (Smolin & Shepelev, 1969), where  $\square$  denotes a cation vacancy, or in  $\text{RE}_{9.33}\square_{0.67}(\text{SiO}_4)_6\text{O}_2$  (RE = La and Sm; Kuz'min & Belov, 1965). If a non-defect structure is assumed, and thus the M site is fully occupied, the compounds must contain some divalent cations, such as in  $\text{Sm}_5(\text{SiO}_4)_3\text{O}$ , where some  $\text{Sm}^{3+}$  ions are reduced to  $\text{Sm}^{2+}$  (Morgan *et al.*, 2002); alternatively, one monovalent cation may replace one

trivalent cation, such as in the title compounds, where one  $\text{Y}^{3+}$  ion is replaced by an  $\text{Na}^+$  or  $\text{Li}^+$  ion. Additional apatite-type compounds are  $\text{Nd}_8\text{Mn}_2(\text{SiO}_4)_6\text{O}_2$  (Klüver & Müller-Buschbaum, 1995) and  $\text{KNd}_9(\text{SiO}_4)_6\text{O}_2$  (Pushcharovskii *et al.*, 1978). Except for the latter (space group  $P6_3$ ), all of the others are in space group  $P6_3/m$ , which is also the symmetry of the parent-phase apatite  $\text{Ca}_5(\text{SiO}_4)_3\text{F}$ .

We present here the structure refinement of the new compound  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  at 100 and 295 K and compare the results with those for  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  and  $\text{Ca}_5(\text{SiO}_4)_3\text{F}$ . The crystal structure of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  was first described by Gunawardane *et al.* (1982). However, since Gunawardane *et al.* (1982) only refined the  $\text{Y}^{3+}$  positions with anisotropic atomic displacement parameters, we also present a re-determination of the structure of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  at 270 and 100 K, giving full anisotropic atomic displacement parameters for all atoms.

The following description of the structures refers predominantly to the data sets for each compound recorded near room temperature. The lattice parameters of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  (at 270 K) are in perfect agreement with those given by Gunawardane *et al.* (1982) for their sample [which has  $a = 9.334(2) \text{ \AA}$  and  $c = 6.759(1) \text{ \AA}$ ]. At room temperature, the  $a$  lattice parameter for  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  is similar to that of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  [ $a = 9.3386(10) \text{ \AA}$ ], whereas the  $c$  parameter is  $0.027 \text{ \AA}$  smaller than that of the sodium compound. Fig. 1 shows the molecular structure of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ , including the atomic nomenclature used in this paper, and Figs. 2 and 3 show polyhedral representations of the structure, viewed along  $[0001]$ . At 295 K, the structure of  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  consists of discrete  $\text{SiO}_4$  tetrahedra, with Si–O distances ranging between  $1.600(6)$  and  $1.623(4) \text{ \AA}$  (Table 1); the mean value is  $1.615(5) \text{ \AA}$ . The bond lengths are very similar to those found for  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  at 270 K [mean Si–O =  $1.618(5) \text{ \AA}$ ; Table 3]. The mean Si–O bond length in the silicate oxyapatite is  $\sim 0.09 \text{ \AA}$  larger than the average P–O bond length in the fluorine apatite ( $1.535 \text{ \AA}$ ; Sundarsanen *et al.*, 1972), thus perfectly reflecting the difference in ionic radii between

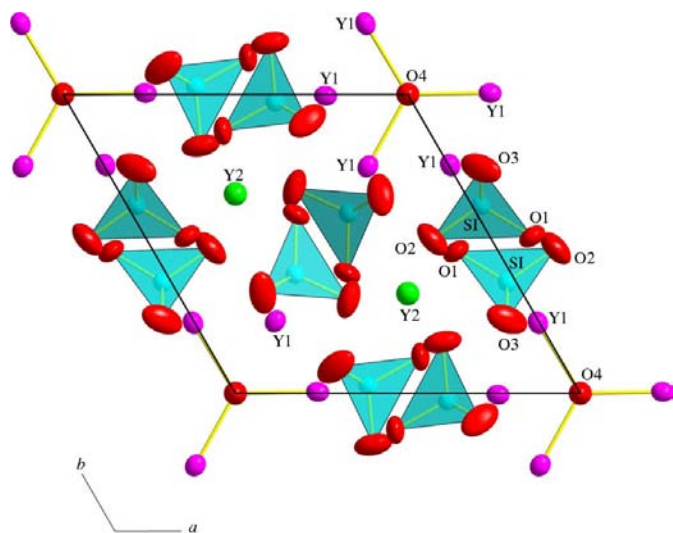


**Figure 1**

A view of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  at 270 K, with displacement ellipsoids at the 95% probability level. [Symmetry codes: (i)  $x, y, \frac{1}{2} - z$ ; (ii)  $1 - x + y, 1 - x, z$ ; (iii)  $x - y, x, -z$ ; (iv)  $x - y, x, \frac{1}{2} + z$ ; (v)  $-y, x - y, z$ ; (vi)  $1 - x, 1 - y, \frac{1}{2} + z$ ; (vii)  $y, 1 - x + y, \frac{1}{2} + z$ ; (viii)  $x, 1 + y, z$ .]

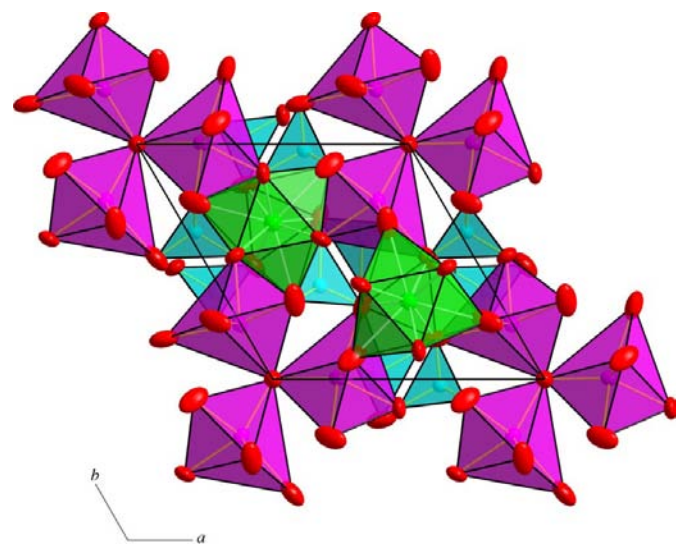
$^{[IV]}\text{Si}^{4+}$  and  $^{[IV]}\text{P}^{5+}$  [0.26 and 0.17 Å, respectively (Shannon & Prewitt, 1969); the first superscript refers to the coordination number of the specific cation]. The bond-length distortion (deviation of individual bond lengths from their mean value; BLD; Renner & Lehmann, 1986) of the  $\text{SiO}_4$  bonds in  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  is small [0.52 (5)%], but it is somewhat larger than that in the sodium compound [0.33 (5)%]. The tetrahedral angle variance (TAV; Robinson *et al.*, 1971), which gives the deviation of individual bond angles from the ideal tetrahedral bond angle ( $109.47^\circ$ ), is slightly smaller [11.8 (2) $^\circ$ ] in the lithium compound [*cf.* 12.6 (2) $^\circ$  for  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ ]. The large TAV values show that the tetrahedron is distinctly distorted; however, this behaviour is observable not only in the two compounds investigated here but also in other silicate oxyapatites. Apatite itself [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ; Sudarsanan *et al.*, 1973] contains regular tetrahedral sites [BLD = 0.20 (5)% and TAV = 3.4 (2) $^\circ$ ], mainly because the  $\text{O3}-\text{P}-\text{O3}(x, y, -z + \frac{1}{2})$  bond angle is much larger (*i.e.* more ideal) in apatite [ $107.4(2)^\circ$ , compared with  $104.0(3)$  and  $103.4(3)^\circ$  in the lithium and sodium oxyapatites, respectively]. The tetrahedral O–O edge opposite the  $\text{O3}-\text{Si}-\text{O3}(x, y, -z + \frac{1}{2})$  angle is common to the tetrahedron and the sevenfold-coordinated Y1 polyhedron, while all four of the tetrahedral corners are also shared with four additional Y1 polyhedra. The small  $\text{O3}-\text{Si}-\text{O3}(x, y, -z + \frac{1}{2})$  bond angle reflects enhanced electrostatic repulsion across the common edge between the tetrahedron and the Y1 site. The edges opposite the  $\text{O1}-\text{Si}-\text{O3}$  angles are common to the tetrahedral site and two neighbouring Y2 polyhedra, and one corner of the tetrahedron is also shared with a third Y2 site. The volume of the tetrahedron in  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  ( $V_{\text{TET}} = 2.15 \text{ \AA}^3$ ) is comparable to that in  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  ( $V_{\text{TET}} = 2.16 \text{ \AA}^3$ ).

Yttrium occupies two different sites, *viz.* Y1 (6*h*) and Y2 (4*f*). The Y atom at 6*h* is coordinated by seven O atoms in a pentagonal bipyramidal geometry (one O1 atom, one O2



**Figure 2**  
A polyhedral representation of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  at 270 K, viewed along [0001]. Only the  $\text{SiO}_4$  tetrahedra are shown for clarity, with displacement ellipsoids at the 95% probability level.

atom, four O3 atoms and one O4 atom; Fig. 3). Atom O4 lies at position 2*a* (with  $z = \frac{1}{4}$  and  $\frac{3}{4}$ ) and fits into the triangular cavity formed by three Y1 atoms (Fig. 2). A close resemblance between the two title compounds and the fluorine apatite is evident here. In  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , the F atom (substituted for the O atom) also lies at position 2*a*. Larger anions, such as  $\text{Cl}^-$  in the chlorine apatite  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ , are found at position 2*b* (with  $z = 0$  and  $\frac{1}{2}$ ). In  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ , the Cl atom, corresponding to atom O4 in the title compounds, is linked to six metal atoms. A central  $\text{Y1O}_7$  polyhedron shares five of its seven corners with other  $\text{Y}^{3+}\text{O}_7$  Y1 polyhedra *via* the four symmetry-related O3 atoms and atom O4. Viewed along the *c* axis, it becomes apparent that three Y1 sites share one central O4 atom at a common corner and are arranged in a trigonal fashion around the hexagonal axis. The O3 atoms are common corners of one Y1 polyhedron, one Y2 polyhedron and one tetrahedron, while atoms O1 and the O2 are common to two Y2 polyhedra and one tetrahedron. In  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  at 295 K, the Y1–O bond distances range between 2.1973 (7) and 2.699 (6) Å [mean 2.380 (4) Å]. This mean value is larger than that in  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  at 270 K [2.366 (4) Å], mainly because the Y1–O2( $-y, x - y, z$ ) bond length [2.700 (7) Å] is much longer in  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  than in the sodium compound [2.634 (5) Å]. Atom O2 lies at the conjunction point of two Y2 polyhedra, one Y1 polyhedron (sharing common edges) and one tetrahedral site (shared corner). The shortest Y1–O bond length is that to the ‘free’ O4 atom, which lies at position 2*a* ( $z = \frac{1}{4}$  and  $\frac{3}{4}$ ). Because the Y1–O2( $-y, x - y, z$ ) bond is longer, the bond-length distortion [3.48 (5)%] is higher for  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  than for  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  [BLD = 3.05 (5)%], and both values are higher than that for fluorine apatite [BLD = 2.48 (5)%; Sudarsanan *et al.*, 1972]. The volumes of the Y1 polyhedra are similar to one another ( $V_{\text{Y1}} = 19.8$  and  $20.0 \text{ \AA}^3$  in the Na and Li compounds, respectively). The average Y–O bond is  $\sim 0.06 \text{ \AA}$  smaller than the average Ca–



**Figure 3**  
A polyhedral representation of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$  at 270 K, viewed along [0001], showing the Y1 and Y2 polyhedra. The Y2 polyhedra are only shown for  $z = \frac{3}{4}$ .

O bond lengths in the fluorine apatite (Sudarsanan *et al.*, 1972), again reflecting the size difference between the  $Y^{3+}$  and  $Ca^{2+}$  ions.

The  $Y^{3+}$  ion, together with the  $Na^+$  or  $Li^+$  ion at the 4f (Y2) position, is coordinated by nine atoms at average distances of 2.502 (5) and 2.521 (5) Å for the lithium and sodium compounds, respectively, forming a tricapped trigonal-prismatic geometry (Fig. 3). A central Y2–O polyhedron shares two common faces (one defined by the three symmetry-related O1 atoms, the other by three symmetry-related O2 atoms) with two neighbouring Y2 polyhedra, forming a face-sharing row in the [0001] direction. In  $LiY_9(SiO_4)_6O_2$  at 295 K, six of the nine Y2–O bonds are between 2.312 (4) and 2.411 (4) Å (those forming shared faces), and the other three are longer [2.782 (6) Å]. The Y2–O bond lengths in  $LiY_9(SiO_4)_6O_2$  are 0.013–0.025 Å shorter than those in  $NaY_9(SiO_4)_6O_2$ . As the row of Y2 polyhedra runs parallel the *c* axis and the  $Li^+$  ion is found on the Y2 site, the fact that the *c* lattice parameter is shorter in  $LiY_9(SiO_4)_6O_2$  than in the sodium analogue can be related directly to the replacement of the larger  $Na^+$  ion by the much smaller  $Li^+$  cation. While the volume of the Y1 site in  $LiY_9(SiO_4)_6O_2$  is similar to that in  $NaY_9(SiO_4)_6O_2$ , the volume of the Y2 polyhedron is somewhat lower [ $V_{Y2} = 29.82$  (1) Å<sup>3</sup> in  $LiY_9(SiO_4)_6O_2$  and  $V_{Y2} = 30.35$  (1) Å<sup>3</sup> in  $NaY_9(SiO_4)_6O_2$ ]. For both compounds, the average Y2–O bond is longer than the average Y1–O bond, mainly because of the different coordination numbers of the two sites and thus the different ionic radii for the  $Y^{3+}$  ion. The O atoms show significant anisotropic vibration, which is most evident for atoms O2 and O3 in both compounds. This result shows that an isotropic description of the O atoms, as given by Gunawardane *et al.* (1982) for  $NaY_9(SiO_4)_6O_2$ , is not appropriate.

Both compounds also adopt  $P6_3/m$  symmetry at 100 K. No change of symmetry takes place. The unit cell of  $LiY_9(SiO_4)_6O_2$  contracts uniformly (by ~0.3%) in both the *a* and the *c* directions. From the available two points (100 and 295 K), a linear thermal-expansion coefficient ( $\alpha = 13.7 \times 10^{-5} K^{-1}$ ) can be estimated for both the *a* and the *c* lattice parameters. These thermal-expansion coefficients are much larger than those of  $NaY_9(SiO_4)_6O_2$ , where  $\alpha$  is  $6.6 \times 10^{-5}$  and  $2.1 \times 10^{-5} K^{-1}$  for the *a* and *c* lattice parameters, respectively. The overall changes in individual and mean bond lengths (Tables 2 and 4) upon cooling are small and, because of the large s.u. values, are only slightly more than 1–2 s.u. Some trends of a more general nature may also be extracted. For both compounds, the average Y2–O bond lengths, as well as the Y2-site polyhedral volumes, show the most significant change (contraction) upon cooling; the Y1–O bonds also contract upon cooling, but to a lesser extent. This behaviour shows the ninefold-coordinated and  $Li^+/Na^+$ -containing site to be more susceptible (less rigid) to temperature changes than the Y1 site. For both compounds, the average Si–O bond is not shortened with decreasing temperature but tends to increase. It has to be kept in mind that the overall changes are small and within 1 s.u. For bond lengths corrected for thermal motion, these effects are even

more pronounced but are still only slightly larger than 1 s.u. At 100 K, the anisotropic atomic displacement parameters are generally smaller than those of the 270 and 295 K structures. For the Y- and Si-atom sites, these parameters decrease uniformly (by ~15%), while for the O-atom sites, these parameters decrease by 20–30%. Atoms O2, O3 and O4 still exhibit large anisotropic vibrations at 100 K.

## Experimental

Single crystals of the title compounds were obtained while attempting to synthesize the clinopyroxene compounds  $LiYSi_2O_6$  and  $NaYSi_2O_6$  using high-temperature solution (flux) growth methods.  $Li_2CO_3$  ( $Na_2CO_3$ ),  $Y_2O_3$  and  $SiO_2$  were mixed in proportions corresponding to the chemical composition of  $LiYSi_2O_6$  ( $NaYSi_2O_6$ ). The carefully ground mixtures and  $Li_2MoO_4$  ( $Na_2MoO_4$ ), serving as the high-temperature solvent (nutrient–flux ratio 1:10), were placed in a covered platinum crucible, heated slowly to 1573 K (1473 K), maintained at this temperature for 24 h and then cooled slowly ( $2 K h^{-1}$ ) to 673 K. As synthesis experiments have shown, the clinopyroxene phases are not stable under these experimental conditions. After removing the high-temperature flux in the case of the lithium compound, the experimental product consisted of colourless prismatic-to-needle-like colourless crystals of  $LiY_9(SiO_4)_6O_2$ . For the  $NaY_9(SiO_4)_6O_2$  compound, the product consisted of colourless cubic crystals of  $Y_2Si_2O_7$  (thortveitite type; Redhammer & Roth, 2003), thin large platelets of  $Na_2Si_2O_5$  and cubic colourless crystals of  $NaY_9(SiO_4)_6O_2$ . Semiquantitative EDX (energy-dispersive X-ray) analysis on the latter crystals using a Zeiss scanning electron microscope revealed the presence of Na, Y, Si and O atoms.

## $LiY_9(SiO_4)_6O_2$ at 295 K

### Crystal data

$LiY_9(SiO_4)_6O_2$   
 $M_r = 1391.76$   
 Hexagonal,  $P6_3/m$   
 $a = 9.3376$  (14) Å  
 $c = 6.7321$  (10) Å  
 $V = 508.34$  (13) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 4.546$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 3117 reflections  
 $\theta = 2.9$ – $27.8^\circ$   
 $\mu = 25.85$  mm<sup>-1</sup>  
 $T = 295$  (1) K  
 Prism, colourless  
 0.16 × 0.08 × 0.08 mm

### Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 via equivalents using *X-SHAPE*  
 and *X-RED* (Stoe & Cie, 1996)  
 $T_{min} = 0.023$ ,  $T_{max} = 0.167$   
 4204 measured reflections

382 independent reflections  
 325 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.091$   
 $\theta_{max} = 26.4^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -11 \rightarrow 11$   
 $l = -8 \rightarrow 8$

**Table 1**

Selected geometric parameters (Å, °) for  $LiY_9(SiO_4)_6O_2$  at 295 K.

Y1–O4	2.1973 (7)	Y2–O1 <sup>v</sup>	2.411 (4)
Y1–O3 <sup>i</sup>	2.266 (4)	Y2–O3 <sup>vi</sup>	2.782 (6)
Y1–O1 <sup>ii</sup>	2.364 (6)	Si–O2	1.600 (6)
Y1–O3	2.432 (4)	Si–O1	1.614 (6)
Y1–O2 <sup>iii</sup>	2.699 (6)	Si–O3	1.623 (4)
Y2–O2 <sup>iv</sup>	2.312 (4)		
O2–Si–O1	113.9 (3)	O1–Si–O3	108.1 (3)
O2–Si–O3	111.1 (2)	O3–Si–O3 <sup>vii</sup>	104.0 (3)

Symmetry codes: (i)  $x - y, x, \frac{1}{2} + z$ ; (ii)  $1 - x + y, 1 - x, z$ ; (iii)  $-y, x - y, z$ ; (iv)  $x, 1 + y, z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vi)  $y, 1 - x + y, \frac{1}{2} + z$ ; (vii)  $x, y, \frac{1}{2} - z$ .

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.031$   
 $wR(F^2) = 0.054$   
 $S = 1.07$   
 382 reflections  
 46 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.013P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.98 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.051 (3)

**LiY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> at 100 K**

## Crystal data

LiY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>  
 $M_r = 1391.76$   
 Hexagonal,  $P6_3/m$   
 $a = 9.3108 (14) \text{ \AA}$   
 $c = 6.7088 (10) \text{ \AA}$   
 $V = 503.67 (13) \text{ \AA}^3$   
 $Z = 1$   
 $D_x = 4.588 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 4980 reflections  
 $\theta = 2.3\text{--}32.1^\circ$   
 $\mu = 26.09 \text{ mm}^{-1}$   
 $T = 100 (1) \text{ K}$   
 Prism, colourless  
 $0.15 \times 0.08 \times 0.07 \text{ mm}$

## Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 via equivalents using *X-SHAPE*  
 and *X-RED* (Stoe & Cie, 1996)  
 $T_{\min} = 0.087$ ,  $T_{\max} = 0.149$   
 4987 measured reflections

508 independent reflections  
 455 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.065$   
 $\theta_{\max} = 29.5^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -12 \rightarrow 12$   
 $l = -8 \rightarrow 9$

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.024$   
 $wR(F^2) = 0.041$   
 $S = 1.16$   
 508 reflections  
 45 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0091P)^2 + 1.5231P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.84 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.77 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0138 (11)

**Table 2**

 Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for LiY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> at 100 K.

Y1—O4	2.1926 (5)	Y2—O1 <sup>v</sup>	2.398 (2)
Y1—O3 <sup>i</sup>	2.255 (3)	Y2—O3 <sup>vi</sup>	2.765 (3)
Y1—O1 <sup>ii</sup>	2.355 (3)	Si—O2	1.606 (3)
Y1—O3	2.423 (3)	Si—O1	1.617 (3)
Y1—O2 <sup>iii</sup>	2.690 (4)	Si—O3	1.624 (3)
Y2—O2 <sup>iii</sup>	2.301 (2)		
O2—Si—O1	113.9 (2)	O1—Si—O3	107.66 (14)
O2—Si—O3	111.39 (12)	O3—Si—O3 <sup>vii</sup>	104.4 (2)

Symmetry codes: (i)  $x - y, x, \frac{1}{2} + z$ ; (ii)  $1 - x + y, 1 - x, z$ ; (iii)  $-y, x - y, z$ ; (iv)  $x, 1 + y, z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vi)  $y, 1 - x + y, \frac{1}{2} + z$ ; (vii)  $x, y, \frac{1}{2} - z$ .

**NaY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> at 270 K**

## Crystal data

NaY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>  
 $M_r = 1407.72$   
 Hexagonal,  $P6_3/m$   
 $a = 9.3386 (10) \text{ \AA}$   
 $c = 6.7589 (8) \text{ \AA}$   
 $V = 510.47 (10) \text{ \AA}^3$   
 $Z = 1$   
 $D_x = 4.579 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 4465 reflections  
 $\theta = 3.1\text{--}32.3^\circ$   
 $\mu = 25.77 \text{ mm}^{-1}$   
 $T = 270 (1) \text{ K}$   
 Cuboid, colourless  
 $0.15 \times 0.14 \times 0.10 \text{ mm}$

## Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 via equivalents using *X-SHAPE*  
 and *X-RED* (Stoe & Cie, 1996)  
 $T_{\min} = 0.031$ ,  $T_{\max} = 0.079$   
 5619 measured reflections

460 independent reflections  
 402 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.087$   
 $\theta_{\max} = 28.2^\circ$   
 $h = -12 \rightarrow 12$   
 $k = -12 \rightarrow 12$   
 $l = -9 \rightarrow 8$

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.035$   
 $wR(F^2) = 0.053$   
 $S = 1.20$   
 460 reflections  
 40 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0113P)^2 + 2.1558P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.87 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0124 (11)

**Table 3**

 Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for NaY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> at 270 K.

Y1—O4	2.2285 (7)	Y2—O1 <sup>v</sup>	2.433 (4)
Y1—O3 <sup>i</sup>	2.267 (4)	Y2—O3 <sup>vi</sup>	2.807 (4)
Y1—O1 <sup>ii</sup>	2.340 (5)	Si—O2	1.607 (5)
Y1—O3	2.414 (4)	Si—O1	1.618 (5)
Y1—O2 <sup>iii</sup>	2.634 (5)	Si—O3	1.623 (4)
Y2—O2 <sup>iv</sup>	2.324 (4)		
O2—Si—O1	113.9 (3)	O1—Si—O3	108.5 (2)
O2—Si—O3	110.97 (18)	O3 <sup>vii</sup> —Si—O3	103.4 (3)

Symmetry codes: (i)  $x - y, x, \frac{1}{2} + z$ ; (ii)  $1 - x + y, 1 - x, z$ ; (iii)  $-y, x - y, z$ ; (iv)  $x, 1 + y, z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vi)  $y, 1 - x + y, \frac{1}{2} + z$ ; (vii)  $x, y, \frac{1}{2} - z$ .

**NaY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> at 100 K**

## Crystal data

NaY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>  
 $M_r = 1407.72$   
 Hexagonal,  $P6_3/m$   
 $a = 9.3274 (10) \text{ \AA}$   
 $c = 6.7554 (7) \text{ \AA}$   
 $V = 508.98 (9) \text{ \AA}^3$   
 $Z = 1$   
 $D_x = 4.593 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 5008 reflections  
 $\theta = 3.1\text{--}32.1^\circ$   
 $\mu = 25.84 \text{ mm}^{-1}$   
 $T = 100 (1) \text{ K}$   
 Cuboid, colourless  
 $0.15 \times 0.14 \times 0.10 \text{ mm}$

## Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 via equivalents using *X-SHAPE*  
 and *X-RED* (Stoe & Cie, 1996)  
 $T_{\min} = 0.027$ ,  $T_{\max} = 0.073$   
 7439 measured reflections

637 independent reflections  
 534 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.086$   
 $\theta_{\max} = 32.1^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -10 \rightarrow 9$

**Table 4**

 Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for NaY<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> at 100 K.

Y1—O4	2.2275 (5)	Y2—O1 <sup>v</sup>	2.425 (3)
Y1—O3 <sup>i</sup>	2.265 (3)	Y2—O3 <sup>vi</sup>	2.797 (4)
Y1—O1 <sup>ii</sup>	2.334 (4)	Si—O2	1.605 (4)
Y1—O3	2.412 (3)	Si—O3	1.624 (3)
Y1—O2 <sup>iii</sup>	2.628 (5)	Si—O1	1.625 (4)
Y2—O2 <sup>iii</sup>	2.325 (3)		
O2—Si—O3	111.05 (15)	O2—Si—O1	114.1 (2)
O3—Si—O3 <sup>vii</sup>	103.7 (2)	O3—Si—O1	108.23 (16)

Symmetry codes: (i)  $x - y, x, \frac{1}{2} + z$ ; (ii)  $1 - x + y, 1 - x, z$ ; (iii)  $-y, x - y, z$ ; (iv)  $x, 1 + y, z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vii)  $x, y, \frac{1}{2} - z$ .

## Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\max} < 0.001$
$R(F) = 0.036$	$\Delta\rho_{\max} = 0.93 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.057$	$\Delta\rho_{\min} = -0.94 \text{ e } \text{\AA}^{-3}$
$S = 1.20$	Extinction correction: <i>SHELXL97</i>
637 reflections	Extinction coefficient: 0.0093 (8)
40 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 1.3664P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

For the refinement of  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ , initial structure solution on the data set at 100 K showed that the compound exhibits the oxyapatite structure type. Two different  $\text{Y}^{3+}$  (*6h* and *4f*), one  $\text{Si}^{4+}$  (*6h*) and four different  $\text{O}^{2-}$  positions were found. Subsequent structure refinements on the absorption-corrected data were performed, in the final stage of which all site occupancies were allowed to vary. A distinct cation deficit was found at the Y2 (*4f*) position, whereas all other positions (including the O-atom positions) showed fully occupied sites within 1 s.u. The occupancy at the Y2 position was 0.254 (corresponding to 3.048  $\text{Y}^{3+}$  atoms per formula unit) instead of the required 0.3333 (4.0  $\text{Y}^{3+}$  atoms per formula unit). For a cation-deficient but charge-balanced compound [ $\text{Y}_{9.33}\square_{0.67}(\text{SiO}_4)_6\text{O}_2$ ], the occupancy at the Y2 site should refine to 0.2778 (3.33  $\text{Y}^{3+}$  atoms per formula unit). It was concluded that the Y2 site is fully occupied, the stoichiometric compound  $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$  has been formed during synthesis and the  $\text{Li}^+$  ion occupies 0.25 of the Y2 (*4f*) site, whereas 0.75 is occupied by the  $\text{Y}^{3+}$  ion. Fixing the occupancies of the Y2 site to the above stoichiometry, but allowing all other sites to vary freely, the final refinement of the site-occupation factors converged to 0.995 (5) (Y1), 0.998 (9) (Si), 1.001 (18) (O1), 1.014 (18) (O2), 0.998 (18) (O3) and 1.00 (2) (O4) at 100 K, and to 1.000 (9) (Y1), 1.007 (14) (Si), 1.00 (2) (O1), 1.01 (2) (O2), 1.01 (3) (O3) and 1.00 (3) (O4) at 295 K. These occupancies confirm a stoichiometric model, and thus all occupancies were fixed at their ideal values for all atoms in the final refinement stage. For the refinement of  $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ , the initial structure model for the data at 100 K consisted of two different  $\text{Y}^{3+}$  sites, one  $\text{Si}^{4+}$  site and four different  $\text{O}^{2-}$  positions. From the structure topology, it was found that the compound belongs to the apatite structure type. The  $\text{Y}^{3+}$  ion is at the *6h* and *4f* positions (instead of  $\text{Ca}^{2+}$  in, for example, fluorine apatite; Sudarsanan *et al.*, 1972, the  $\text{Si}^{4+}$  ion is at *6h* (instead of  $\text{P}^{5+}$ ), and atom O4 is found in the *2a* position (instead of F). Subsequent structure refinements showed distinct cation deficits at the *4f* position (3.08  $\text{Y}^{3+}$  atoms per formula unit instead of the 4.0 required). The deficit, however, was larger than expected for a charge-balanced cation-defect oxyapatite (3.33 atoms per formula unit). From semiquantitative EDX analysis it was found that the compound contains a significant number of  $\text{Na}^+$  ions, which

in turn occupy the *4f* position ( $0.25 \text{ Na}^+ + 0.75 \text{ Y}^{3+}$ ). Refinements were also performed in which the site occupation of the *4f* position was fixed; however, the occupancies of successive sites were allowed to vary. These refinements converged to site-occupation values of 1.036 (8) (Y1), 1.006 (12) (Si), 1.019 (8) (O1), 1.043 (8) (O2), 1.043 (9) (O3) and 1.056 (8) (O4) at 100 K. As these results support a stoichiometric model, all occupancies were fixed at their ideal values in the final refinement stage.

For both compounds at all temperatures, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

GJR acknowledges financial support from the Austrian Academy of Science *via* an APART (Austrian Program for Advanced Research and Technology) scholarship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1182). Services for accessing these data are described at the back of the journal.

## References

- Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Release 2.1b. Crystal Impact GbR, Bonn, Germany.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gunawardane, R. P., Howie, R. A. & Glasser, F. P. (1982). *Acta Cryst.* **B38**, 1564–1566.
- Klüver, E. & Müller-Buschbaum, Hk. (1995). *Z. Naturforsch. Teil B*, **50**, 61–65.
- Kuz'Min, E. A. & Belov, N. V. (1965). *Dokl. Akad. Nauk SSSR*, pp. 88–90.
- Morgan, M. G., Wang, M. & Mar, A. (2002). *Acta Cryst.* **E58**, i70–i71.
- Pushcharovskii, D. Y., Dorokhova, G. I., Pobedimskaya, E. A. & Belov, N. V. (1978). *Dokl. Akad. Nauk*, **242**, 835–838.
- Redhammer, G. J. & Roth, G. (2003). *Acta Cryst.* **C59**, i103–i106.
- Renner, B. & Lehmann, G. (1986). *Z. Kristallogr.* **175**, 43–59.
- Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.
- Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* **B25**, 925–934.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Smolin, Yu. I. & Shepelev, Yu. F. (1969). *Izv. Akad. Nauk SSSR Neorg. Mater.* **5**, 1823–1825.
- Stoe & Cie (1996). *X-SHAPE* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (2002). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Sudarsanan, K., Mackie, P. E. & Yaing, R. A. (1972). *Mater. Res. Bull.* **7**, 1331–1338.
- Sudarsanan, K., Young, R. A. & Donnay, J. D. H. (1973). *Acta Cryst.* **B29**, 808–814.
- White, T. J. & ZhiLi, D. (2003). *Acta Cryst.* **B59**, 1–16.