Structure of the Oxyapatite NaY$_9$(SiO$_4$)$_6$O$_2$

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Abstract. NaY$_9$Si$_6$O$_{26}$, hexagonal, $a = 9.334$ (2), $c = 6.759$ (1) Å, space group $P6_3/m$, $Z = 1$. Structure refinement was carried out by the block-diagonal least-squares method to $R = 0.071$ with 500 unique reflections. The structure is shown to be very similar to that of fluorapatite, apart from the replacement of fluoride by oxide and disorder in the arrangement of Na and Y on the 4(f) cation sites. The 6(h) cation sites are occupied exclusively by yttrium.

Introduction. A large number of compounds having the apatite structure and possessing the general formula $M_{10}(XO_4)_6Z_2$ occur in nature or have been synthesized. Many are listed by Corbridge (1974) together with unit-cell parameters and a drawing of the structure. Although the Z position is commonly occupied by F, Cl or OH, oxyapatites containing O in the Z position also occur. Charge balance is maintained in various ways: for example Smolin & Shepelev (1969) determined the structure of a lanthanoid oxyapatite and found that lanthanoid atoms were omitted; thus the formula was Gd$_{9.33}\square_{0.67}$(SiO$_4$)$_6$O$_2$, where $\square$ denotes a cation vacancy. Cation defects can also occur with divalent-ion substitution, as was shown by Hata, Marumo, Iwai & Aoki (1980) in their study of a Pb^{2+} apatite. Less is known about the structure of cation-stoichiometric oxyapatites, of which NaY$_9$(SiO$_4$)$_6$O$_2$ may be considered to be a typical representative. Yet the structure is of considerable interest because of the luminescent properties of suitably activated oxyapatites. Attempts based on crystal-field theory have been made to explain the luminescence, but these presuppose a knowledge of the cation-site population and environment. Felsche (1972, 1973) used plots of the lattice parameters vs the radius of Ln^{3+} in apatites in the series M^+Ln$_9$(SiO$_4$)$_6$O$_2$ (M = Li, Na) to deduce that the Na was in 6(h). On the other hand, Blase (1975), using a local-charge-compensation model, deduced that the Na was occupying 4(f) sites: however, his reasoning presupposed that the 'free' O, *i.e.* the O not belonging to any XO$_4$ tetrahedron, was situated in trigonally coordinated sites at $z = \frac{1}{4},\frac{3}{4}$ on the hexagonal axis.

Experimental. Conditions for the growth of single crystals were determined from liquidus data on the system Na$_2$O–Y$_2$O$_3$–SiO$_2$ (Lee, Marr & Glasser, 1981). On account of the high fusion point of Y-apatite, crystals were grown from a melt having the composition (in mol%) Na$_2$O = 30, Y$_2$O$_3$ = 10, SiO$_2$ = 60. The batch composition, prepared from pure (>99.9%) oxide or carbonate percursors, was melted at 1748 K and quenched to yield a glass. This glass was annealed in air at 1538 K for 12 h in a platinum crucible. After quenching, it consisted of well faceted apatite crystals in glass. A stout hexagonal prism about 0.1 × 0.1 × 0.3 mm was isolated under the petrographic microscope and used for measurements.

The unit cell was initially established from X-ray powder data, which was clearly characteristic of the apatite type and gave unit-cell parameters virtually identical to those reported by Ito (1968). The intensity data were collected on a Nicolet P3 four-circle diffractometer using Mo radiation and a graphite monochromator ($\lambda = 0.71069$ Å). Intensities were obtained for 500 unique reflections ($\theta/2\theta$ scan method) for $2\theta < 60°$, $I > 3\sigma$. The instrument was permitted to vary the scan rate in relation to the intensity being measured. No absorption corrections were applied. Calculations were carried out on the Honeywell 66/80 computer of the University Computing Centre. The programs were those of Ahmed, Hall, Pippy & Huber (1973) modified for use on this computer by one of us (RAH) and J. S. Knowles of the University of Aberdeen. In least-squares refinements, unit weights were used throughout; scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Initially all atoms were placed in the positions given by Wyckoff (1960) for fluorapatite: Y in place of Ca [on 6(h) and 4(f)], Si in place of P [on 6(h)] and O in place of F [on 2(a)]. Least-squares refinements using these atomic positions led to $R = 0.17$, but no further refinement was possible and the Si—O bond distances were unsatisfactory. Therefore, some O atoms [O(1), O(2) and O(3)] bonded to Si were omitted: a structure-factor calculation based on the remaining

Table 1. *Positional and thermal parameters of* $NaY_9Si_6O_{26}$

	No. of atoms per unit cell	x	y	z	B_{iso} (Å²)	Occupancy factor
O(1)	12	0·2486 (10)	0·3389 (11)	0·4380 (15)	1·19 (13)	1·000
O(2)	6	0·4868 (15)	0·3171 (15)	0·2500	0·98 (18)	1·000
O(3)	6	0·5252 (14)	0·4013 (14)	0·7500	0·83 (17)	1·000
Si	6	0·3723 (5)	0·3994 (5)	0·2500	0·26 (5)	1·000
Y(1)	6	0·2375 (2)	0·0042 (2)	0·2500	0·706*	1·000
Y(2)†	4	0·3333	0·6666	−0·0019 (3)	0·711*	0·750
O(4)	2	0·0000	0·0000	0·2500	1·2 (3)	1·00

Anisotropic temperature factors for yttrium‡

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Y(1)	0·0030 (2)	0·0034 (2)	0·0022 (2)	0·000	0·000	0·0029 (3)
Y(2)	0·0034 (4)	0·0034 (5)	0·0019 (4)	0·000	0·000	0·0034 (12)

* B_{iso} values of the Y atoms were calculated from the anisotropic thermal parameters.

† $Y(2) \equiv (Y_{0.75}Na_{0.25})$.

‡ Thermal vibration correction is of the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + klB_{23} + hlB_{13} + hkB_{12})]$.

Table 2. *Bond lengths* (Å) *and angles* (°)

SiO₄ tetrahedra

Si–O(1)	(×2)	1·62 (1)	Si–O(3)		1·61 (1)
Si–O(2)		1·60 (2)			

O(1)–Si–O(2)		111·4 (6)	O(3)–Si–O(1)		108·2 (6)
O(2)–Si–O(3)		113·7 (6)	O(1)–Si–O(1)		103·6 (5)

Y–O polyhedra

Y(1)–O(1)	(×2)	2·29 (1)	Y(2)–O(1)	(×3)	2·78 (1)
Y(1)–O(1)	(×2)	2·41 (1)	Y(2)–O(2)	(×3)	2·32 (1)
Y(1)–O(2)		2·67 (1)	Y(2)–O(3)	(×3)	2·42 (1)
Y(1)–O(3)		2·37 (1)			
Y(1)–O(4)		2·20 (1)			

atoms followed by Fourier synthesis gave an electron density map from which improved coordinates for O(1–3) were obtained. In addition, it was noted at this stage that the isotropic temperature factor for Y(2) [in 4(f)] was very much higher than that of Y(1) [in 6(h)]. In relation to the chemical formula, this was interpreted to mean that the 6(h) sites were fully occupied by Y and that the remaining atoms (three Y and one Na) were distributed over the 4(f) sites. Placing the 'free' O atom, O(4), at height $z = 0,\frac{1}{2}$ worsened the R factor, and this O was accordingly left at $z = \frac{1}{4},\frac{3}{4}$ on the c axis. Block-diagonal least-squares refinement was therefore continued with the appropriate new O positions, with Y atoms on 6(h) sites and with Y atoms of 4(f) sites given an occupancy of 0·75 and with O(4) at $z = \frac{1}{4},\frac{3}{4}$. This yielded $R = 0·079$. Refinement was completed with Y atoms allowed to vibrate anisotropically, whereby $R = 0·071$ was obtained.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36602 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, CH1 2HU, England.

The final positional parameters are presented in Table 1. Acceptable bond lengths and angles were achieved (Table 2); moreover, a difference map exhibited no significant features and the distribution of ΔF^2 over $\sin^2 \theta$ and over $|F_o|$ was essentially uniform.

Discussion. The structure found for $NaY_9Si_6O_{26}$ may be compared with those of other apatites. There are two independent positions for metal atoms in the unit cell. The Y(1) atom which occupies the 6(h) position is coordinated by seven O atoms. O(4) atoms fit into the cavities of the triangles formed from three Y(1) atoms. In this respect, the structure closely resembles that of fluorapatite rather than that of chlorapatite, in which the Cl corresponding to O(4) is instead linked to six metal atoms. In Y-apatite, each Y(1) is linked to O(2), O(3), and four O(1) at a mean distance of 2·42 Å while it is linked to O(4) at a relatively short distance of 2·20 Å. The second set of crystallographically independent Y positions, Y(2), along with O atoms form six parallel columns around the central 6_3 axis. These Y(2) atoms are surrounded by nine O atoms [three O(1), three O(2) and three O(3)] at a mean distance of 2·40 Å. A more detailed examination of bond lengths (Table 2) discloses that six of these O atoms are at shorter distances [three O(2) and three O(3) at ~2·37 Å] while the remaining three O(1) atoms are at a greater distance (~2·78 Å). Although the Na required by the chemical formula was never explicitly included in the calculations, the site occupancy of 0·75 adopted for Y(2) in 4(f) is clearly compatible with the presence in the same sites of Na with occupancy 0·25. Although the chemical evidence, based upon the phase purity of $Na_2O–Y_2O_3–SiO_2$ compositions, indicates that Y-apatite can tolerate a significant Na deficiency, the cation substructure of crystals obtained from Na-rich melts is believed to be essentially complete. The 'free' O atom lies at heights $z = \frac{1}{4},\frac{3}{4}$. In this respect it occupies the same positions as F in fluorapatite. The alternative arrangement, with O(4) at $z = 0,\frac{1}{2}$, as occurs with Cl in chlorapatite, does not occur. The consequence of restricting the O position to $\frac{1}{4},\frac{3}{4}$ c is that satisfactory electrostatic charge balance can only be achieved by restricting occupancy of the 6(h) sites to Y, thereby forcing the Na to occupy 4(f) sites. In this respect we agree completely with Blase's (1975) analysis of the electrostatic balances attained in the two models he considered, concluding that Na on 4(f) sites was favoured. However, it is not impossible to suppose that if a larger X^{2-} ion, e.g. S^{2-}, could be substituted in the structure, it would instead occupy sites at $z = 0,\frac{1}{2}$ thereby altering the electrostatic balance and resulting in a concomitant redistribution of the Na and Y population.

OXYAPATITE $NaY_9(SiO_4)_6O_2$

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Structure du Trisulfure de Lanthane et de Gallium

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Abstract. $LaGaS_3$, monoclinic, $P2_1/b$, $a = 10.33$ (9), $b = 12.82$ (6), $c = 10.56$ (4) Å, $\gamma = 98.90$ (7)°, $Z = 12$. The structure has been solved by direct methods and refined by a least-squares procedure to a final R value of 0.0571 for 3185 reflections collected with an automatic four-circle diffractometer (Mo $K\alpha$). The gallium atoms have tetrahedral coordination. One lanthanum atom is nine-coordinated and the two others eight-coordinated.

Introduction. $LaGaS_3$ se forme facilement en chauffant La_2S_3 et Ga_2S_3 en proportions stoechiométriques à 1153 K. Mais les dimensions des cristaux obtenus dans ces conditions sont insuffisantes pour une étude cristallographique et d'autres phases apparaissent en même temps.

La préparation de monocristaux de $LaGaS_3$ a été réalisée à partir d'un verre par l'un de nous (CD), la cristallisation se produisant au cours de son recuit.

Le sulfure La_2S_3 est obtenu par union directe des éléments et le sulfure Ga_2S_3, par action d'un courant de H_2S sur l'oxyde GaOOH, dans des conditions qui éliminent toute trace d'oxygène. La manipulation de ces deux sulfures est effectuée en atmosphère d'azote sec. Le mélange, de composition $7La_2S_3 + 9Ga_2S_3$, est introduit dans une ampoule de silice à parois très minces, recouvertes intérieurement de carbone miroitant, dans laquelle le vide est fait avant scellement. On chauffe d'abord à 1713 K, température à laquelle se produit la combinaison, puis à 1423 K pendant une heure, afin d'obtenir un liquide homogène. Par trempe

brutale de l'ampoule et de son contenu dans du mercure refroidi à 243 K, on obtient un produit vitreux.

Ce verre est finalement recuit pendant deux semaines à 1198 K dans un creuset de carbone vitreux disposé dans une ampoule de silice scellée sous vide. L'excès de sulfure de gallium introduit au début, donne naissance à un liquide assurant la croissance en son sein de cristaux transparents et incolores de $LaGaS_3$.

Cette nouvelle phase n'est pas celle décrite par Loireau-Lozac'h, Guittard & Flahaut (1976, 1977) pour $LaGaS_3$ au cours de leur étude du diagramme $La_2S_3–Ga_2S_3$.

Le cristal isolé pour cette étude se présente sous la forme d'un petit parallélépipède d'environ $80 \times 80 \times 110$ μm. Sa taille est suffisamment petite pour qu'il soit possible de négliger son pouvoir absorbant vis à vis des rayons X ($\mu l = 1,8$ pour $K\alpha$ du molybdène dans sa plus grande dimension).

Le réseau est monoclinique.

Les extinctions systématiques: $k = 2n + 1$ pour les réflexions $hk0$ et $l = 2n + 1$ pour les réflexions $00l$, conduisent à un seul groupe possible $P2_1/b$ centrosymétrique.

Les intensités de 3185 réflexions, telles que $2\theta < 55°$, non nulles, indépendantes par symétrie, ont été enregistrées à l'aide d'un diffractomètre à quatre cercles Syntex. On utilise un balayage sur $\omega–2\theta$, 2θ variant de $2\theta_1 - 0,70°$ à $2\theta_2 + 0,70°$, θ_1 et θ_2 étant respectivement les angles de diffraction correspondant aux longueurs d'onde $K\alpha_1$ et $K\alpha_2$ du molybdène. Les intensités ont été corrigées des facteurs de Lorentz et de polarisation.