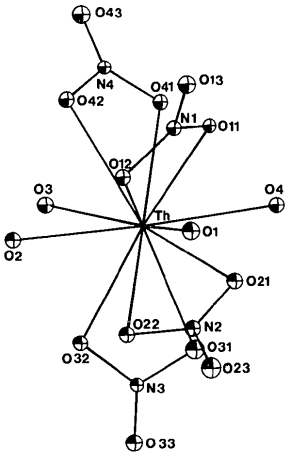

Fig. 1. Représentation *ORTEP* (Johnson, 1976) de l'unité moléculaire.

gène. L'étude par diffraction de neutrons (Taylor *et al.*, 1966) a mis en évidence deux types de liaison hydrogène intermoléculaire: des liaisons fortes avec des distances O(eau libre)—O(eau liée au thorium) de l'ordre de 2,70 Å et des liaisons plus faibles, O(eau libre)—O(nitrate) de 2,90 Å. Une recherche de telles liaisons intra et intermoléculaires effectuée sur le tétrahydrate à partir des distances oxygène—oxygène a montré l'existence de liaisons hydrogène intramoléculaires fortes entre les molécules d'eau liées à l'atome de thorium [O(1)—O(3) 2,75 (2) Å, O(1)—O(4) 2,70 (2) Å] et de liaisons hydrogène intermoléculaires faibles possibles entre les molécules d'eau et les oxygènes des nitrates [O(1)—O(42) 2,98 (2) Å, O(2)—O(22) 2,87 (2) Å].

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Structure of a New Mini-Laser Material, $K_3NdSi_2O_7$*

BY M. S. HWANG AND H. Y.-P. HONG

Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan

AND M. C. CHENG AND Y. WANG†

Department of Chemistry, National Taiwan University, Taipei, Taiwan

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Abstract. $M_r = 2574$, hexagonal, $P6_3/mcm$, $a = 10{\cdot}025$ (1), $c = 14{\cdot}526$ (1) Å, $V = 1264{\cdot}1$ (3) Å^3, $Z = 6$, $D_x = 3{\cdot}387$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, μ(Mo $K\alpha$) = 7·945 mm^{-1}, $F(000) = 1206$, $T = 298$ K, final $R = 0{\cdot}0308$ for 1417 observed reflections. The crystal structure consists of columns of discrete Si_2O_7 units formed by two SiO_4 tetrahedra sharing one corner. There are two types of NdO_6 polyhedra: an octahedron and a trigonal prism. The SiO_4 and NdO_6 polyhedra are linked to form a rigid three-dimensional network in which K^+ ions are situated in the interstitial positions. The shortest Nd—Nd distance is 5·7878 (6) Å and no bridging O atom is found between any two Nd atoms. Therefore, this material appears to be a promising candidate for an efficient mini-laser crystal.

Introduction. Initially, laser action involving Nd^{3+} fluorescence was observed only in host materials exhibiting severe concentration quenching, *i.e.* high amounts of Nd^{3+} in the host silicate crystal. However, Danielmeyer & Weber (1972) found that concentration quenching is greatly reduced in neodymium pentaphosphate, NdP_5O_{14}. Laser action has also been obtained in several compounds with reduced con-

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† To whom all correspondence should be addressed.

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centration quenching such as $NdLiP_4O_{12}$ (Hong, 1975), $KNdP_4O_{12}$ (Chinn & Hong, 1975), $NdAl_3(BO_3)_4$ (Chinn & Hong, 1975) and $K_3Nd(PO_4)_2$ (Hong & Chinn, 1976). It has been shown (Hong & Dwight, 1974) that the degree of concentration quenching in Nd laser materials is determined by the linkage between the NdO_y polyhedra. In all the laser compounds mentioned above, the NdO_y polyhedra are isolated from each other; there are no bridging O^{2-} ions. We synthesized a new Nd compound, $K_3NdSi_2O_7$. Its crystal structure was determined by single-crystal X-ray diffraction to elucidate whether it has isolated NdO_y polyhedra. Our results confirm that this is, indeed, the case.

Experimental. A mixture of Nd_2O_3, SiO_2, K_2CO_3, KCl and KF with a large excess of the latter three compounds was placed in an alumina crucible and heated to 1423 K and held for 4 h. The temperature was decreased at a rate of 6 K h^{-1} from 1423 to 1123 K and then the furnace was turned off. After being washed with hot water, hexagonal-shaped crystals were obtained.

Crystal 0·065 × 0·065 × 0·35 mm. CAD-4 diffractometer. Unit-cell dimensions from 24 reflections with $30{\cdot}26 \le 2\theta \le 34{\cdot}1°$. Monochromated Mo $K\alpha$ radiation. $2\theta_{max} = 120°$. h, k 0–24 ($k < h$); l 0–35. Variation of three standard reflections monitored every 30 min <3%. 3789 unique reflections, 1417 observed with $I \ge 3\sigma(I)$. $R = 3{\cdot}08\%$, $wR = 2{\cdot}44\%$, $S = 1{\cdot}75$. Data corrected for Lp effect. Absorption correction made by Gaussian integration with eight measured faces and 10 × 10 × 10 grid points, transmission factors 0·28–0·44. Weighting scheme from counting statistics. $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = \sigma^2(I)/4F_o^2$. Structure solved by heavy-atom method. $(\Delta/\sigma)_{max} = 0{\cdot}22$. The maximum peak on final $\Delta\rho$ map = 2·2 e Å^{-3} near K. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Computing programs: NRCC *SDP* PDP-11 package (Gabe & Lee, 1981).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Selected interatomic distances and angles are listed in Table 2.

The crystal structure is illustrated in Fig. 1 as a projection on the *ab* plane. It is composed of columns of discrete $Si_2O_7^{6-}$ units parallel to **c**, the $Si_2O_7^{6-}$ unit being formed by two SiO_4^{2-} tetrahedra sharing a corner. There are two unique Nd atoms and three K atoms in the structure. Nd(1) and K(2) form a column along 0,0,z with alternate K and Nd atoms at a distance of $\frac{1}{4}c$. In these columns Nd(1) can be described as surrounded by six O atoms in a trigonal pyramidal fashion as shown by the dashed lines in Fig. 1. Nd(2) and K(1) form another column along $\frac{1}{3},\frac{2}{3},z$ again with alternate

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $K_3NdSi_2O_7$

	Site symmetry	x	y	z	B_{eq}*
Nd(1)	$\bar{6}2m$	0	0	$\frac{1}{4}$	0·42 (2)
Nd(2)	312	$\frac{2}{3}$	$\frac{1}{3}$	0	0·43 (1)
K(1)	$\bar{6}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	1·44 (6)
K(2)	$\bar{3}1m$	0	0	0	1·38 (11)
K(3)	m	0·3304 (2)	0·3304 (2)	0·5898 (1)	1·53 (5)
Si	m	0·6594 (2)	0·6594 (2)	0·6437 (1)	0·49 (4)
O(1)	m	0·1795 (3)	0·1795 (3)	0·1432 (2)	1·00 (11)
O(2)	$m2m$	0·6012 (4)	0·6012 (4)	$\frac{3}{4}$	1·19 (16)
O(3)	1	0·6780 (3)	0·1522 (3)	0·0941 (1)	1·27 (12)

* $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *for* $K_3NdSi_2O_7$

Around Nd		Nd–Nd distances	
Nd(1)–O(1) (6×)	2·375 (5)	Nd(1)–Nd(1)	7·2628 (6)
Nd(2)–O(3) (6×)	2·321 (5)	Nd(1)–Nd(2)	6·8326 (6)
		Nd(2)–Nd(2)	5·7878 (6)
Around K		Around Si	
K(1)–O(2) (3×)	3·066 (9)	Si–O(1)	1·615 (3)
K(1)–O(3) (6×)	2·941 (2)	Si–O(2)	1·651 (1)
K(2)–O(1) (6×)	2·751 (3)	Si–O(3) (2×)	1·611 (6)
K(3)–O(1) (2×)	2·975 (5)	O(1)–Si–O(2)	110·9 (2)
K(3)–O(3) (2×)	2·801 (7)	O(1)–Si–O(3)	110·8 (1)
K(3)–O(3) (2×)	3·027 (4)	O(2)–Si–O(3)	107·0 (1)
K(3)–O(3) (2×)	3·056 (3)	O(3)–Si–O(3)	110·2 (3)

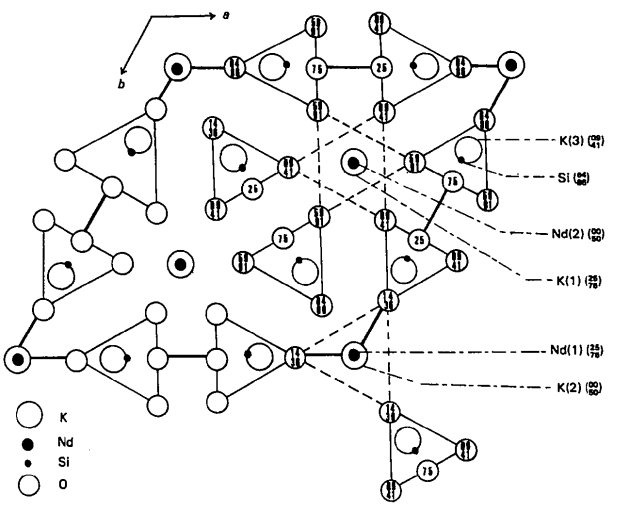

Fig. 1. The crystal structure projected on the *ab* plane. The numbers in circles and parentheses are z coordinates (×10^2) of O atoms and other atoms respectively.

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43822 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms at distances of $\frac{1}{4}c$; however, Nd(2) is surrounded octahedrally by six O atoms from Si_2O_7 units. K(3) ions are between the Si_2O_7 units along $0,\frac{1}{3},z$. The K–O distances are longer than the sum of ionic radii of K and O (2·7 Å). All Nd–O polyhedra are isolated from each other with no bridging O atoms between Nd atoms. Therefore concentration quenching will be reduced in this compound. It has been shown (Hong & Dwight, 1974) that laser action is determined by the probability of electric-dipole transitions between certain orbitals of Nd^{3+}, which is highly dependent on the deviation from inversion symmetry around the Nd ion. Based on this argument, Nd(1) cannot produce laser action because it has $\bar{1}$ symmetry. However, Nd(2) could produce strong laser action because it is at a site with 32 symmetry.

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Cubic Structure of Chromium Iodine Boracite

BY A. MONNIER, G. BERSET AND H. SCHMID

Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland

AND K. YVON

Laboratoire de Cristallographie aux Rayons-X, Université de Genève, 24 quai E. Ansermet, CH-1211 Geneva 4, Switzerland

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Abstract. $Cr_3B_7O_{13}I$, $M_r = 566{\cdot}56$, cubic, $F\bar{4}3c$, $a = 12{\cdot}214\ (1)$ Å, $V = 1822{\cdot}1\ (5)$ Å^3, $Z = 8$, $D_x = 4{\cdot}130$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 2·44 mm^{-1}, $F(000) = 2112$, $T = 298$ K, final $R = 0{\cdot}023$ for 109 unique reflexions with $I \geq 3\sigma(I)$; shortest interatomic distances (Å): [Cr–O] = 2·075 (2), [Cr–I] = 3·0520 (2), [O–B] = 1·439 (3), [O–O] = 2·393 (3). The deviation from planarity of the O-atom environment around the metal atom is compared with those of other cubic boracites.

Introduction. Boracites, $M_3B_7O_{13}X$ (M = bivalent metal ion, X = halogen ion), tend to undergo structural phase transitions (Schmid, 1965; Nelmes, 1974; Toledano, Schmid, Clin & Rivera, 1985). A structural feature of particular interest is the environment of the metal ions because it is relatively invariant with respect to the substitution of other metal and halogen ions whereas it changes strongly during phase transitions. In the cubic high-temperature modification the metal ions are surrounded by a deformed square-planar oxygen-ion configuration whereas in the trigonal, orthorhombic and monoclinic low-temperature modifications a halogen atom joins the coordination sphere thus leading to a fivefold, approximately square-pyramidal, non-metal configuration (Nelmes, 1974; Ito, Morimoto & Sadanaga, 1951; Abrahams, Bernstein & Svensson, 1981; Rivera, 1978). Despite extensive structural work (for reviews see Nelmes & Thornley, 1974; Nelmes & Hay, 1981) the reasons for this abrupt change in coordination are not yet clear.

The purpose of this study was to refine the cubic structure of a further member of this series and to compare its metal environment with those of other cubic boracites. Chromium iodine boracite, $Cr_3B_7O_{13}I$ (hereafter Cr–I), which remains cubic down to at least 4 K, appeared to be a favorable compound for such a comparison because structure data are available for its chlorine-based congener $Cr_3B_7O_{13}Cl$ (Nelmes & Thornley, 1974).

Experimental. Cubic crystals (edge length ≃0·05 mm) of blue-green colour were obtained by a gas-phase transport technique (Schmid, 1965; Schmid & Tippmann, 1979). Data collection: Philips PW1100 diffractometer, graphite monochromator, one hemi-

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