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Structure of the Nd U-Phase, $Nd_3Al_{3\cdot5}Si_{2\cdot5}O_{12\cdot5}N_{1\cdot5}$; a Nitrogen-Containing Phase of the $La_3Ga_5GeO_{14}$ Structure Type

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Abstract. $Nd_3Al_{3\cdot5}Si_{2\cdot5}O_{12\cdot5}N_{1\cdot5}$, $M_r = 818\cdot4$, trigonal, $P321$, $a = 7\cdot974\,(2)$, $c = 4\cdot875\,(1)$ Å, $V = 268\cdot5\,(2)$ Å^3, $D_x = 5\cdot06$ g cm^{-3}, $Z = 1$, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 149\cdot9$ cm^{-1}, $F(000) = 371$, $T = 293$ K, $R = 0\cdot034$ for 864 unique observed reflections. The Nd U-phase of aluminium neodymium silicon oxynitrides occurs in rare-earth sialon ceramics as a crystalline grain-boundary phase. Single crystals were obtained by heat treating mixtures of Si_3N_4, SiO_2, Al_2O_3 and Nd_2O_3 at 1550 K in a nitrogen atmosphere. The structure is of the $La_3Ga_5GeO_{14}$ structure type and exhibits layers of corner-sharing M(O,N)$_4$ (M = Al, Si), tetrahedra interconnected by Al(O,N)$_6$ octahedra. The Nd atoms are located between the tetrahedral layers and are eight-coordinated by (O,N) atoms at distances 2·315 (5)–2·757 (4) Å. The observed M—(O,N) bond distances indicate a partially ordered distribution of Al and Si atoms in the structure.

Introduction. Materials based on a solid solution of aluminium and oxide ions, into both α- and β-Si_3N_4, represent an important group of structural ceramics, named sialons (Slasor, Liddell & Thompson, 1986). One advantage of sialon materials is that they can often be compacted to full density by pressureless sintering. The pressureless technique requires some kind of sintering aid, however, and various oxides such as Y_2O_3, Nd_2O_3, MgO, CaO and BeO have been used for this purpose (Ekström, 1990). Since the sintering aid cannot be incorporated into the sialon phases, except to a very small extent in the α-sialon phase, it will for the most part end up at the grain boundaries, either as a glass or as secondary crystalline phase(s). Frequently, such grain-boundary phases will deteriorate the high-temperature properties of the ceramic; its capacity to withstand high-temperature (> 1270 K) oxidation might, for instance, be seriously affected. Therefore, it is of interest to find sintering additives with a minimal influence on the high-temperature performance. The search for, and the structural characterization of, intergranular phases formed in various sialon systems are thus of great interest in designing sialon ceramic materials with specific properties.

A crystalline intergranular phase, named U-phase, was first reported to occur in the Nd-, Ce- and Y-sialon systems (Spacie, Lidell & Thompson, 1988). The U-phase has since been found in other sialon systems, and its composition, as determined by energy dispersive X-ray (EDX) analyses, corresponds to $Ln_3Al_{3+x}Si_{3-x}O_{12+x}N_{2-x}$, with Ln = La, Ce, Nd, Sm, Gd, Dy and $0 \le x \le 1$. The structure of the Nd U-phase was recently determined from X-ray powder data using the Rietveld technique (Käll, Grins, Olsson, Lidell, Korgul & Thompson, 1990) and was found to be isotypic with $La_3Ga_5GeO_{14}$ (Kaminskii, Mill, Belokoneva & Khodzhabagyan, 1983). Since the structure determination was based on powder data, however, the light-atom positions obtained were of limited accuracy. In particular, one of the M—(O,N) (M = Al, Si) bond distances came out unrealistically short and was therefore fixed at a credible value in the final refinements. Furthermore, it was not possible to deduce a plausible distribution of Al and Si atoms in the structure from the data. The present single-crystal study of the Nd U-phase structure has thus been made in order to determine

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Table 1. *Experimental conditions for the crystal structure determination of* $Nd_3Al_{3.5}Si_{2.5}O_{12.5}N_{1.5}$

Crystal shape (mm)	Irregular, 0·06 × 0·035 × 0·025
Crystal size (mm³)	4.8×10^{-5}
Intensity data collection	
Max. $\sin(\theta)/\lambda$ (Å^{-1})	0·993
Range of h, k and l	$-13 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 9$
Standard reflections	3
Intensity instability (%)	< 4·7
Number of measured reflections	1465
Number of unique reflections	1320
R_{int}	0·018
Number of observed unique reflections	864
Criterion for significance	$I > 3\sigma(I)$
Absorption correction	Numerical integration
Linear absorption coefficient (cm^{-1})	149·9
Transmission factor range	0·54–0·78
Structure refinement	
Minimization of	$\Sigma w(\Delta F)^2$
Anisotropic thermal parameters	Nd, Al, Si and O
Number of refined parameters	38
Weighting scheme	$w = 1/[\sigma^2(\lvert F \rvert)]$
Final R	0·034
wR	0·023
wR for all reflections	0·025
S	1·27
$(\Delta/\sigma)_{max}$	0·003
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	−1·7 and +1·9

the light-atom positions more accurately and to obtain information about the distribution of the light atoms in the structure.

Experimental. *Synthesis.* Powders of Si_3N_4, SiO_2, Al_2O_3 and Nd_2O_3 were mixed according to the formula $Nd_3Al_{3+x}Si_{3-x}O_{12+x}N_{2-x}$, with $0 \le x \le 1$. The mixtures were pelletized, heat-treated at 1550 K for 40 h and then cooled to room temperature at a rate of 1 K min^{-1}. Guinier–Hägg photographs showed that all preparations contained the Nd U-phase as major crystalline constituent together with smaller amounts of $NdAlO_3$. The largest fraction of U-phase was observed in the sample with $x = 0.5$. A scanning electron microscope study of the latter sample revealed that U-phase crystals with sizes up to 200 μm had been formed and that the sample also contained an appreciable amount of a glass phase.

Composition. The Al:Si atomic ratio in the Nd U-phase crystals was determined by EDX microanalysis using a JEOL 820 SEM equipped with a Link 10000 EDX system. Part of the sample with composition $x = 0.5$ was plane polished and a series of EDX-point analyses were made on different embedded U-phase crystals, yielding Al:Si = 1·418 (12). This Al:Si ratio corresponds to $x = 0.52$ (2), implying an approximate composition of $Nd_3Al_{3.5}Si_{2.5}O_{12.5}N_{1.5}$.

Data collection and correction for absorption. X-ray diffraction data were collected on a Stoe–AED2 diffractometer; experimental conditions are listed in Table 1. ω–2θ scan mode used, with $\Delta\omega = 1°$ and scan speed 0·3–0·6° min^{-1}. Cell parameters determined from 14 reflections in the range $37.5 \le 2\theta \le 45.8°$, yielding $a = 7.974$ (2) and $c = 4.875$ (1) Å, agreeing well with cell dimensions obtained from Guinier–Hägg data $a = 7.974$ (1) and $c = 4.873$ (1) Å. Intensities were corrected for background, polarization and Lorentz effects.

Due to irregular crystal shape the following procedure was used in absorption correction. The supported crystal was coated with a thin conducting layer of gold by sputtering and a series of 12 micrographs were recorded using a JEOL 820 scanning electron microscope. To approximate the crystal shape 14 points on the crystal surface were selected, with one point that was clearly defined in all micrographs chosen as the origin. Space coordinates of the points were calculated from their positions in the micrographs.† Points were used to calculate 13 surface planes, approximating the crystal shape. Surface planes were assigned Miller indices based on the orientation of the crystal in the diffractometer. Correction for absorption was then carried out using numerical Gauss integration. The validity of the correction was checked by correcting 12 ψ scans recorded at $75 < \chi < 89°$ and $13 < 2\theta < 71°$.

Structure refinement. The refinements were made in space group $P321$ (No. 150), using *SHELX76* (Sheldrick, 1976) and X-ray scattering factors for neutral atoms, including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974, Vol. IV). The atomic coordinates obtained in the previous powder study (Käll *et al.*, 1990) were used as starting coordinates. Initial isotropic refinements with both Al,Si atoms and O,N atoms statistically distributed over their available sites yielded the residuals $R = 0.056$ and $wR = 0.051$ for intensity data not corrected for absorption and $R = 0.039$ and $wR = 0.029$ for absorption-corrected data. Although the distribution of Al and Si atoms could not be discerned on the basis of their X-ray scattering powers, a probable distribution was deduced at this stage from the M—O bond distances and was then used in the final refinements (*cf.* Table 2 and below). The N atoms could not be allocated to any specific positions and a statistical distribution of O and N atoms was hence assumed. Anisotropic temperature factors were allowed in the final refinement, and an empirical extinction correction was applied with $|F_c^*| = |F_c|(1 - 10^{-4} \times F_c^2/\sin\theta)$, refined $x =$

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† Lists of structure factors, powder diffraction data (ICDD No. 42-1485), anisotropic displacement parameters, and a description of the calculation of space coordinates for points on a crystal surface from SEM micrographs of the crystal have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54194 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates and isotropic thermal parameters* ($\times 10^4$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Wyckoff position	x	y	z	U_{eq}(Å^2)
Nd	3e	4139 (1)	0	0	91 (1)
Al	1a	0	0	0	97 (9)
Si	2d	$\frac{1}{3}$	$\frac{2}{3}$	5389 (6)	78 (6)
M	3f	7574 (4)	0	$\frac{1}{2}$	114 (8)
O1	2d	$\frac{1}{3}$	$\frac{2}{3}$	2043 (13)	108 (14)
O2	6g	4624 (8)	3044 (7)	3243 (7)	140 (19)
O3	6g	2205 (7)	898 (7)	7606 (9)	183 (20)

The O-atom sites are all assumed partially occupied by N atoms with O:N = 25:3 and the M-atom site by both A1 and Si atoms with Al:Si = 5:1.

Table 3. *Representative bond lengths* (Å) *with e.s.d.'s in parentheses*

AlO_6 octahedron		SiO_4 tetrahedron	
Al—O3 6 ×	1·925 (5)	Si—O1	1·631 (7)
O3—O3^i	2·643 (9)	Si—O2^{iv} 3 ×	1·666 (6)
O3—O3^{ii} 2 ×	2·652 (8)	O1—O2^{iv} 3 ×	2·759 (7)
O3—O3^{iii}	2·951 (9)	O2^{iv}—O2^v 2 ×	2·644 (10)
MO_4 tetrahedron		Nd—O polyhedron	
M^{vi}—O3^{iv} 2 ×	1·707 (4)	Nd—O3^{vii} 2 ×	2·315 (5)
M—O2^{iv} 2 ×	1·785 (6)	Nd—O2^{viii} 2 ×	2·511 (4)
		Nd—O1^{ix} 2 ×	2·601 (3)
O3—O3^{iv}	3·117 (9)	Nd—O2 2 ×	2·757 (4)
O2—O2^{iv}	2·774 (10)	All others > 3·73	
O3—O2^{iv}	2·731 (7)		
O3—O2	2·806 (6)		

Symmetry code: (i) $x-y, -y, 2-z$; (ii) $-y, x-y, z$; (iii) $y, x, 2-z$; (iv) $y, x, 1-z$; (v) $x-y, 1-y, 1-z$; (vi) $1-x+y, 1-x, z$; (vii) $x-y, -y, 1-z$; (viii) $1-y, x-y, z$; (ix) $x, y-1, z$.

The O-atom sites are all assumed partially occupied by N atoms with O:N = 25:3 and the M-atom site by both A1 and Si atoms with Al:Si = 5:1.

2·6 (2) 10^{-3}. The corresponding residuals were $R = 0·034$ and $wR = 0·023$. The final atomic coordinates and selected bond distances are given in Table 2* and Table 3, respectively.

It should be noted that the overall Al:Si ratio in $Nd_3Al_{3·5}Si_{2·5}O_{12·5}N_{1·5}$ was determined by EDX analysis only and could not be substantiated by the structure refinement, as varying the x value in $Nd_3Al_{3+x}Si_{3-x}O_{12+x}N_{2-x}$ between 0 and 1 yielded no significant changes in the R index.

Discussion. The structure of the Nd U-phase is illustrated in Fig. 1. It can be regarded as a framework structure built up of corner-sharing tetrahedra and octahedra containing the Al and Si atoms. The larger Nd atoms are located within cavities in the framework. The framework contains layers, perpendicular to the c axis, of corner-sharing tetrahedra with the M atoms in two sites with Wyckoff notations 2d and 3f in the space group $P321$. The layers are interconnected by octahedra with the central atom in Wyckoff position 1a. The 2d tetrahedron has three corners in common with different 3f tetrahedra, while the fourth corner is not coordinated to any unit of the framework. The 3f tetrahedron has two corners in common with different 2d tetrahedra and two in common with 1a octahedra. The tetrahedral layer containing Al and Si atoms is according to the crystal chemical classification of silicates (Liebau, 1985) an open-branched vierer single layer. The Nd atoms coordinate to eight O atoms, at distances 2·315 (5)–2·757 (4) Å, forming a distorted cubic antiprism. A similar coordination of Nd is observed in the melilite structure (Belokoneva & Belov, 1981).

The N atoms could not be allocated to any specific sites and were thus assumed to be randomly distributed over available sites with an O:N ratio of 25:3. A probable distribution of M = Al,Si atoms over the sites 1a, 2d and 3f can be inferred from the observed M—O distances. The M—O distance in the 1a octahedron is 1·925 (5) Å, an expected value for an Al$^{[6]}$—O bond. The mean M—O distance is 1·66 Å for the 2d tetrahedron, r.m.s. deviation 0·02 Å, and 1·75 Å for the 3f tetrahedron. Assuming that the octahedral 1a site is occupied only by Al atoms and the formula $Nd_3Al_{3·5}Si_{2·5}O_{12·5}N_{1·5}$, determined with

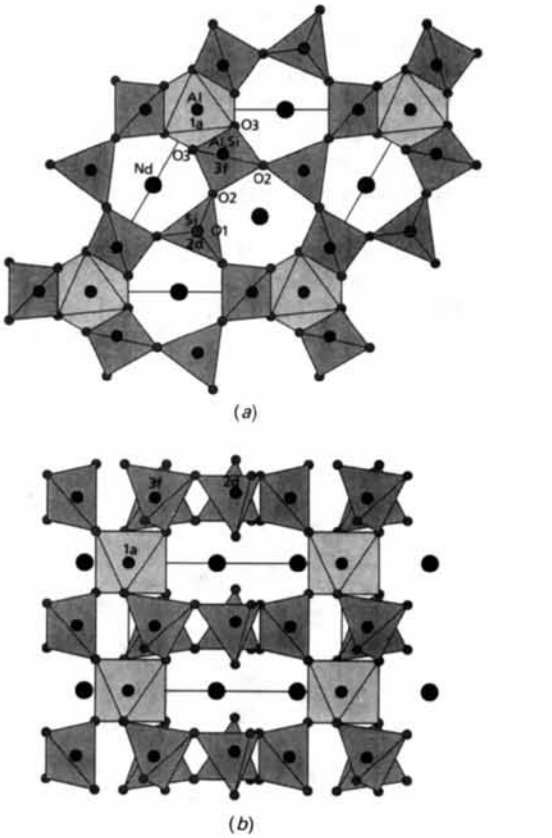

Fig. 1. An illustration of the $Nd_3Al_{3·5}Si_{2·5}O_{12·5}N_{1·5}$ structure viewed down (*a*) [001] and (*b*) [210].

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* See deposition footnote.

EDX, the 2*d* and 3*f* tetrahedral sites are occupied by a total of 2·5 Al and 2·5 Si atoms per unit cell. The considerably shorter mean *M*—O distance observed for the 2*d* tetrahedron compared with the 3*f* tetrahedron suggests that the 2*d* sites are occupied preferentially by the Si atoms and the 3*f* sites by Al and Si atoms in the ratio 5:1. A probable approximate distribution of Al and Si atoms in the structure is thus $Nd_3(Al)^{1a}(Al_{2\cdot5}Si_{0\cdot5})^{3f}(Si_2)^{2d}O_{12\cdot5}N_{1\cdot5}$, with the Wyckoff-site notation superscripted. Summation of effective ionic radii in oxides (Shannon, 1976), using the above distribution of atoms and the observed coordination number of the O atoms, yields bond distances 1·90, 1·63 and 1·73 Å for the sites 1*a*, 2*d* and 3*f*, respectively. The observed bond distances are all slightly longer, which may be due to the O atom positions being partly occupied by the comparatively larger N atoms (Bauer, 1987). A calculation of empirical bond valencies (Brown & Altermatt, 1985) from the structural data, using the distribution of atoms deduced above and the assumed stoichiometry, gives bond-valence sums of +2·95 for Al at site 1*a*, +3·77 for Si at site 2*d*, +3·16 for (Al,Si) at site 3*f* and +2·75 for Nd. However, it can not be ruled out that the 2*d* sites are also occupied, to a smaller extent, by Al atoms. Allowing for this, the structural formula may be written as $Nd_3^{[8ap]}Al^{[6o]}$-$\{\mathbf{uB},4,1^2_\infty\}[(Si,Al)_2^{[4t]}(Al,Si)_3^{(4t)}(O_{12\cdot5}N_{1\cdot5})]$ (Lima-de-Faria, Hellner, Liebau, Makovicky & Parthé, 1990).

An *ORTEP* (Johnson, 1976) drawing of part of the structure is given in Fig. 2, illustrating the anisotropic thermal vibrations of the atoms. The O atoms vibrate approximately perpendicularly to their *M*—O bond directions. The central *M* atom in the 3*f* tetrahedron shows a larger and more anisotropic thermal ellipsoid than the other *M* atoms.

The present refinement of the Nd U-phase structure confirms the structure model previously derived from powder data. The atomic positions and bond distances obtained from the single-crystal data are, as expected, much more accurate. In particular, the unrealistically short Si—O1 bond distance (1·2–1·3 Å) obtained in the Rietveld refinement is amended to the observed value 1·631 (7) Å by the present single-crystal refinement.

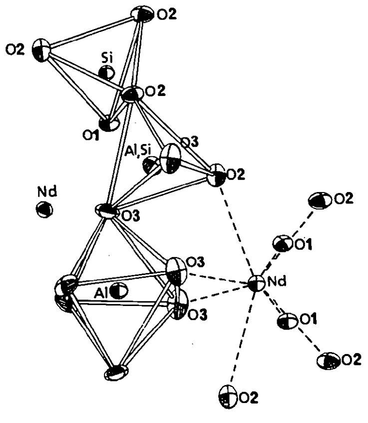

Fig. 2. An *ORTEP* (Johnson, 1976) drawing of part of the $Nd_3Al_{3\cdot5}Si_{2\cdot5}O_{12\cdot5}N_{1\cdot5}$ structure. The thermal vibration ellipsoids enclose an 80% probability distribution.

A compound exhibiting the $La_3Ga_5GeO_{14}$ structure type was first found in the CaO–Ga_2O_3–GeO_2 system, where the phase $Ga_3Ga_2Ge_4O_{14}$ was identified (Mill, Butashin, Ellern & Maier, 1981). The structure type is adopted by a series of oxide phases and allows multiple ion substitutions (Mill, Butashin, Khodzhabagyan, Belokoneva & Belov, 1982). The Ca atoms can thus be replaced by atoms such as Na, Sr, Ba, Pb, La, Pr and Nd and the octahedrally and/or tetrahedrally coordinated Ga and Ge atoms by *e.g.* Cr, Fe, Ni, Al, Si, Mg and Zn.

These isostructural oxide phases exhibit different distributions of the smaller *M* metal atoms over the sites 1*a*, 2*d* and 3*f* (Kaminskii, Belokoneva, Mill, Pisarevskii, Sarkisov, Silvestrova, Butashin & Khodzhabagyan, 1984). In general, however, the 2*d* sites are found to be occupied by the *M* atoms with the smallest radius. The distribution of Al and Si atoms in the Nd U-phase structure deduced above, $Nd_3(Al)^{1a}(Al_{2\cdot5}Si_{0\cdot5})^{3f}(Si_2)^{2d}O_{12\cdot5}N_{1\cdot5}$, can accordingly be interpreted as the smaller Si atoms preferring to occupy the tetrahedral 2*d* sites and Al the octahedral 1*a* site.

The U-phase is the first known case of an oxynitride phase adopting the $La_3Ga_5GeO_{14}$ structure type. Attempts to synthesize a pure oxide U-phase with composition $Ln_3Al_5SiO_{14}$, (Ln = Y, La and Nd) were unsuccessful, as expected from previous findings that compounds with the $La_3Ga_5GeO_{14}$ structure type do not form in the Ln_2O_3–Al_2O_3–SiO_2 systems (Mill, Butashin, Khodzhabagyan, Belokoneva & Belov, 1982). It is therefore concluded that the U-phase is stabilized by its small nitrogen content. A speculative reason for this would be that the structure is stabilized by the occupancy of the 2*d* sites by the smaller Si atoms, which is only stoichiometrically possible if N is added according to $Nd_3Al_{3+x}Si_{3-x}O_{12+x}N_{2-x}$ with $x \leq 1$.

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Structure of Hexaaquacopper(II) Bromate

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Abstract. $[\mathrm{Cu(H_2O)_6}](\mathrm{BrO_3})_2$, $M_r = 427{\cdot}44$, cubic, $Pa\bar{3}$, $a = 10{\cdot}3240\,(6)$ Å, $V = 1100{\cdot}38\,(4)$ Å^3, $Z = 4$, $D_x = 2{\cdot}580\ \mathrm{g\ cm^{-3}}$, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 92{\cdot}32\ \mathrm{cm^{-1}}$, $F(000) = 828$, $T = 296$ K, $R = 0{\cdot}038$ for 336 unique reflections having $I > \sigma_I$. The single type of copper ion (site symmetry $\bar{3}$) is coordinated by six water-molecule O atoms, each at an observed distance of 2·079 (4) Å, in an array which is virtually regular octahedral, the nominal 90° angles measuring 89·95 (15) and 90·05 (15)°. Thus, this is not a typical Cu$^{\rm II}$ complex in which (consistent with a static Jahn–Teller effect) a distorted octahedral array displays '(2 + 2 + 2)' coordination; rather, it is the sixth strict example of a Cu$^{\rm II}$ static structure inconsistent with the Jahn–Teller theorem. The presence of a dynamic Jahn–Teller effect is supported by the data. The single type of bromate ion has an observed Br—O bond length 1·649 (3) Å and O—Br—O bond angle 104·17 (15)°. The bromate ion was found to manifest rigid-body behavior but, consistent with a dynamic Jahn–Teller effect, the copper–oxygen complex did not. The Br—O bond length corrected for rigid-body motion is 1·663 Å. Refinement of the positional parameters of the two inequivalent H atoms permitted a detailed analysis of hydrogen bonding, which occurs principally between the oxygen octahedra and the bromate groups. This structure is isomorphic with those of hexaaquanickel(II) chlorate, hexaaquacobalt(II) bromate and hexaaquanickel(II) bromate, all of which have been reported recently from this laboratory. It is of interest that a tetrahydrated phase crystallized at room temperature from a saturated aqueous copper(II) chlorate solution, whereas a hexahydrated phase crystallized from a saturated aqueous copper(II) bromate solution treated in the same manner.

Introduction. Our interest in a structural study of $[\mathrm{Cu(H_2O)}_x](\mathrm{BrO_3})_2$ was greatly stimulated by the finding that the chlorate analogue, when crystallized from a saturated aqueous solution at room temperature, forms a tetrahydrated phase (Blackburn, Gallucci & Gerkin, 1991*a*). A hexahydrated phase had been expected since other divalent transition-metal halates obtained in a similar fashion formed hexahydrated phases and information given about copper(II) halates suggested that a stable hexahydrated phase exists for the chlorate compound as well as for the bromate compound. Thus this study was pursued both to determine which phase of the bromate would be observed, and to determine its structure.

Experimental. Hexaaquacopper(II) bromate crystals were obtained by evaporation at room temperature of a solution formed by the metathetical reaction of aqueous analytical reagent-grade copper(II) sulfate with a slight excess of aqueous barium bromate (Strem chemicals) followed by filtration of the barium sulfate precipitate. A clear light-blue crystal with approximate principal dimensions 0·27 × 0·27 ×

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