

Four Cl(1) and four Cl(2) ions form a distorted cube around the Rb⁺ ion located on the $\bar{4}$ axes as shown in Fig. 2. The average distance between the Rb⁺ and Cl⁻ ions, 3.374 Å, is similar to that between the NH₄⁺ and Cl⁻ ions in 2NH₄Cl·CuCl₂·2H₂O, 3.364 Å (Bhakay-Tamhane *et al.*, 1980). The average distance between the K⁺ and Cl⁻ ions in 2KCl·CuCl₂·2H₂O, 3.320 Å (Chidambaram *et al.*, 1970), is shorter than those between the monovalent cation and Cl⁻ ion in the 2RbCl·CuCl₂·2H₂O and 2NH₄Cl·CuCl₂·2H₂O crystals. Since the ionic radii reported for the ions with eight coordination are 1.51, 1.61 (Shannon, 1976) and 1.66 Å (Khan & Baur, 1972) for K⁺, Rb⁺ and NH₄⁺, respectively, the interionic distances estimated by using 1.81 Å for the ionic radius of Cl⁻ (Shannon, 1976) become 3.32, 3.42 and 3.47 Å for the K⁺—Cl⁻, Rb⁺—Cl⁻ and NH₄⁺—Cl⁻ pairs, respectively. For 2KCl·CuCl₂·2H₂O, the average K⁺—Cl⁻ distance measured is comparable to the sum of the ionic radii thus calculated, although the average distances between the

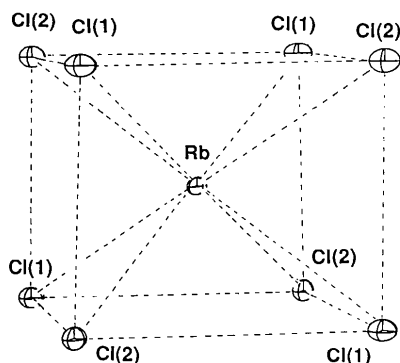


Fig. 2. An ORTEP drawing (Johnson, 1965) of the surroundings of the Rb⁺ ion with the thermal ellipsoids scaled at the 30% probability level.

monovalent cation and Cl⁻ ion for 2RbCl·CuCl₂·2H₂O and 2NH₄Cl·CuCl₂·2H₂O are significantly shorter than the sum of the relevant ionic radii. Judging from the above M⁺—Cl⁻ distances, the ionic radius of the K⁺ ion may be most suitable to occupy the space of the three-dimensional network consisting of [CuCl₄·2H₂O] octahedra and the hydrogen bonds.

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Structures of SrV₆O₁₁ and NaV₆O₁₁

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Abstract. Strontium hexavanadate, SrV₆O₁₁, $M_r = 569.26$, hexagonal, $P6_3/mmc$, $a = 5.7716$ (1), $c = 13.0793$ (5) Å, $V = 377.32$ (2) Å³, $Z = 2$, $D_x = 5.010$ g cm⁻³, $\mu = 137.58$ cm⁻¹, $F(000) = 528.0$, final $R = 0.060$ for 488 unique observed reflections;

sodium hexavanadate, NaV₆O₁₁, $M_r = 504.63$, hexagonal, $P6_3/mmc$, $a = 5.7123$ (1), $c = 13.0974$ (4) Å, $V = 370.12$ (1) Å³, $Z = 2$, $D_m = 4.50$, $D_x = 4.528$ g cm⁻³, $\mu = 71.64$ cm⁻¹, $F(000) = 474.0$, final $R = 0.017$ for 580 unique observed reflections.

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Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$, room temperature. O and Sr (or Na) atoms form a hexagonal close-packed structure and one of the V atoms is situated in its trigonal-bipyramidal cavity. The other V atoms are surrounded octahedrally by six O atoms. The compounds are essentially isostructural with $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$, related compounds of $\text{BaFe}_{12}\text{O}_{19}$ (magnetoplumbite structure).

Introduction. DeRoy, Besse, Chevalier & Gasperin (1987) synthesized $\text{NaV}_6\text{O}_{11}$ for the first time by electrolytic reduction of molten NaVO_3 and described its structure in the asymmetric space group $P\bar{6}2c$. $\text{NaV}_6\text{O}_{11}$ was also obtained by a solid-state reaction and was shown to be a metallic conductor perpendicular to [001] with an anomaly at around 64 K corresponding to a magnetic transition (Kanke, Takayama-Muromachi, Kato & Matsui, 1990). It also shows a metallic conductivity parallel to [001] and exhibits uniaxial spontaneous magnetization parallel to [001] below 64.2 K. The spontaneous magnetization of $\text{NaV}_6\text{O}_{11}$ at 5 K was $1.7 \mu_B$ per formula unit (Uchida, Kanke, Takayama-Muromachi & Kato, 1991).

$\text{SrV}_6\text{O}_{11}$ and $\text{SrT}_x\text{V}_{6-x}\text{O}_{11}$ ($T = \text{Ti, Cr and Fe}$) have been found. The T ions do not localize at a particular site in $\text{SrT}_x\text{V}_{6-x}\text{O}_{11}$ phases (Kanke, Izumi, Takayama-Muromachi, Kato, Kamiyama & Asano, 1990). The structure of $\text{SrV}_6\text{O}_{11}$ has not yet been refined.

In this work, the structures of $\text{NaV}_6\text{O}_{11}$ and $\text{SrV}_6\text{O}_{11}$ were determined in space group $P6_3/mmc$. Their structures are discussed in comparison with those of $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$, $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$ (Cadée & Ijdo, 1984) and $\text{BaFe}_{12}\text{O}_{19}$ (Townes, Fang & Perrotta, 1967).

Experimental. $\text{Sr}_2\text{V}_2\text{O}_7$ and V_2O_3 were mixed in 1:3 molar ratio. The mixture was sealed in a platinum capsule and heated at 1473 K for 1 d. The product was a mixture of $\text{SrV}_6\text{O}_{11}$ and an unknown colorless substance. Crystals of $\text{SrV}_6\text{O}_{11}$ were hexagonal plate shaped, flat in (001). Typical size was 0.2 mm in diameter and 0.1 mm in thickness. Specimen for the intensity collection: hexagonal plate with edge lengths 0.10 (100), 0.11 ($\bar{1}00$), 0.13 (010), 0.12 ($0\bar{1}0$), 0.06 ($1\bar{1}0$), and 0.07 mm ($\bar{1}10$); 0.10 mm thick along [001].

NaVO_3 and V_2O_3 were mixed in a 4:1 molar ratio. The mixture was placed in a gold capsule and sealed in a silica tube, then heated at 923 K for 2 d. The hygroscopic product was ground in air, dried in nitrogen atmosphere at 423 K for 30 min, and then fired in the same manner at 963 K for 4 d. The final product was a mixture of $\text{NaV}_6\text{O}_{11}$, α' - $\text{Na}_x\text{V}_2\text{O}_5$ and an unknown colorless hygroscopic substance. Crystals of $\text{NaV}_6\text{O}_{11}$ were hexagonal plate shaped, flat in

(001). Typical size was 0.6 mm in diameter and 0.2 mm in thickness. Specific gravity was measured by pycnometry using CCl_4 . Specimen for intensity collection: cut into size $0.20 \times 0.17 \times 0.08 \text{ mm}$ (along [140], $[3\bar{2}0]$ and [001], respectively).

An Enraf-Nonius CAD-4 diffractometer was used for data collection with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were determined from 22 reflections ($82 < 2\theta < 90^\circ$). Intensity collection was by ω - θ scan with $\Delta\omega = (0.8 + 0.35\tan\theta)^\circ$, $(\sin\theta/\lambda) < 0.9949 \text{ \AA}^{-1}$, for both $\text{SrV}_6\text{O}_{11}$ and $\text{NaV}_6\text{O}_{11}$.

$\text{SrV}_6\text{O}_{11}$: ($0 \leq h \leq 5$, $0 \leq k \leq 9$, $-26 \leq l \leq 26$, $|h| \leq |k|$) and ($-5 \leq h \leq 0$, $-9 \leq k \leq -1$, $-26 \leq l \leq 26$, $|h| \leq |k|$) for 2480 reflections measured; 389 unobserved. The 2480 measured reflections were averaged into 645 unique reflections, R_{int} (for F) = 0.020, of which 488 reflections had $I > 3\sigma(I)$. Three standard reflections (600, $\bar{4}80$ and $0,0,12$), measured every 4 h, decreased in intensity by 0.4% during the total exposure time of 161.1 h; a linear decay correction was applied. An absorption correction, correction factor for F from 1.782 to 2.610, was applied.

$\text{NaV}_6\text{O}_{11}$: ($0 \leq h \leq 5$, $0 \leq k \leq 9$, $-26 \leq l \leq 26$, $|h| \leq |k|$) and ($-5 \leq h \leq -1$, $-9 \leq k \leq -1$, $-26 \leq l \leq 26$, $|h| \leq |k|$) for 2061 reflections measured; 138 unobserved. The 2061 measured reflections were averaged into 633 unique reflections, R_{int} (for F) = 0.016, of which 580 reflections had $I > 1.5\sigma(I)$. Three standard reflections (600, $\bar{4}80$ and $0,0,12$), measured every 4 h, decreased in intensity by 0.7% during the total exposure time of 137.3 h; a linear decay correction was applied. An absorption correction, correction factor for F from 1.343 to 1.765, was applied.

Both structures were refined by the least-squares method based on F , using anisotropic temperature factors.* Atomic scattering factors ($f = f_o + \Delta f' + i\Delta f''$) for neutral atoms were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs: *SDP* (B. A. Frenz & Associates, Inc., 1985) and *ORTEPII* (Johnson, 1976).

$\text{SrV}_6\text{O}_{11}$: $P6_3/mmc$, $R = 0.060$, $wR = 0.118$, $w = 1/\sigma^2(F)$, 24 parameters refined, $\Delta/\sigma < 0.005$ in the final refinement cycle, $-4.43 \leq \Delta\rho \leq 7.24 \text{ e \AA}^{-3}$.

$\text{NaV}_6\text{O}_{11}$: $R = 0.017$, $wR = 0.031$, $w = 1/\sigma^2(F)$, 26 parameters refined, $\Delta/\sigma < 0.005$ in the final refinement cycle, $-1.33 \leq \Delta\rho \leq 0.97 \text{ e \AA}^{-3}$.

Discussion. The atomic fractional coordinates and the equivalent isotropic thermal parameters are listed in Table 1. The cell constants and the selected inter-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55056 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions in Wyckoff notations, positional parameters, and equivalent isotropic thermal parameters (\AA^2) of SrV₆O₁₁ and NaV₆O₁₁

$$B_{\text{eq}} = (8/9)\pi^2[4U(1,1) + 4U(2,2) + 3U(3,3) - 4U(1,2)].$$

		SrV ₆ O ₁₁	NaV ₆ O ₁₁
V(1)		6g	6g
	B_{eq}	0.53 (2)	0.481 (3)
V(2)		4e	4e
	B_{eq}	0.1460 (1)	0.14754 (2)
	z	0.36 (1)	0.418 (3)
V(3)		2d	2d
	B_{eq}	1.33 (4)	0.467 (3)
O(1)		12k	12k
	x	0.1763 (4)	0.17052 (6)
	z	0.0823 (3)	0.08043 (5)
	B_{eq}	0.56 (7)	0.563 (8)
O(2)		6h	6h
	x	0.1501 (7)	0.15273 (9)
	B_{eq}	0.76 (8)*	0.67 (1)
O(3)		4f	4f
	z	0.5886 (8)	0.59075 (8)
	B_{eq}	1.1 (1)	0.444 (9)
Sr, Na		2c	2c
	B_{eq}	0.42 (1)	2.24 (2)

For both compounds: V(1) $x = 0.5, y = 0, z = 0$; V(2) $x = 0, y = 0$; V(3) $x = \frac{1}{3}, y = \frac{2}{3}, z = \frac{3}{4}$; O(1) $y = 2x$; O(2) $y = 2x, z = \frac{3}{4}$; O(3) $x = \frac{1}{3}, y = \frac{2}{3}$; Sr, Na $x = \frac{1}{2}, y = \frac{1}{2}, z = \frac{1}{4}$.

* Refined isotropically.

Table 2. Cell constants and equivalent interatomic distances (\AA) of SrV₆O₁₁, NaV₆O₁₁, BaTi₂Fe₄O₁₁, BaSn₂Fe₄O₁₁ and BaFe₁₂O₁₉

	SrV ₆ O ₁₁	NaV ₆ O ₁₁	BaTi ₂ - Fe ₄ O ₁₁ *	BaSn ₂ - Fe ₄ O ₁₁ *	BaFe ₁₂ - O ₁₉ †
a	5.7716 (1)	5.7123 (1)	5.8470 (2)	5.9624 (5)	5.893
c	13.0793 (5)	13.0974 (4)	13.6116 (9)	13.7468 (14)	23.194
$M(1)-O(1)$	1.945 (3) × 4	1.9410 (4) × 4	1.997 (4) × 4	2.010 (3) × 4	1.928 (5) × 2 2.106 (4) × 2
$M(1)-O(3^b)$	2.029 (6) × 2	2.0327 (6) × 2	1.997 (4) × 2	2.052 (3) × 2	1.977 (5) × 1 2.091 (6) × 1
Mean $M(1)-O$	1.973	1.9716	1.997	2.024	2.023
$M(2)-O(1)$	1.949 (2) × 3	1.9024 (3) × 3	1.933 (7) × 3	1.998 (5) × 3	1.975 (8) × 3
$M(2)-O(2^b)$	2.026 (1) × 3	2.0210 (2) × 3	2.105 (8) × 3	2.163 (4) × 3	2.060 (7) × 3
Mean $M(2)-O$	1.988	1.9617	2.019	2.081	2.018
$M(3)^\ddagger-O(2)$	1.832 (6) × 3	1.7869 (6) × 3	1.867 (5) × 3	1.907 (5) × 3	1.886 (10) × 3
$M(3)-O(3^{iv})$	2.11 (1) × 2	2.086 (1) × 2	2.098 (14) × 1	2.044 (10) × 1	2.170 (11) × 1 2.583 (14) × 1
$A-O(1)$	2.697 (3) × 6	2.7436 (5) × 6	2.828 (4) × 6	2.842 (4) × 6	2.865 (6) × 6
$A-O(2^b)$	2.891 (4) × 6	2.8595 (5) × 6	2.928 (4) × 6	2.987 (4) × 6	2.952 (1) × 6
Mean $A-O$	2.794	2.8016	2.878	2.915	2.909
$M(2)-M(2^b)$	2.721 (3)	2.6840 (4)	2.904 (22)	3.002 (8)	2.778 (1)
$M(3)-M(3^v)$	0	0	0.485 (24)	0.559 (17)	0.312 (20)

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

*Cadée & Ijdo (1984); $P6_3/mmc$.

† Townes, Fang & Perrotta (1967); $P6_3/mmc$, not isostructural with the others.

‡ Occupied by Fe³⁺ in BaTi₂Fe₄O₁₁ and BaSn₂Fe₄O₁₁ (Cadée & Ijdo, 1984).

§ Inapplicable to BaFe₁₂O₁₉.

atomic distances of the title phases and the related phases are shown in Table 2. Fig. 1 shows the structure of NaV₆O₁₁; SrV₆O₁₁ is isostructural with it. The O atoms form hexagonally close-packed layers parallel to (001). A quarter of the O atoms in every third layer are substituted by Sr or Na atoms.

The Sr and Na atoms are coordinated by 12 O atoms. Between the remaining two O layers, three quarters of octahedral sites (not on the cell edges along [001]) are occupied by V atoms [$M(1)$ sites]. Between the O layer and the Sr,Na-containing O layer, a quarter of octahedral sites (on the cell edges along [001]) are occupied by V atoms [$M(2)$ sites]. A remaining one sixth of the V atoms are placed in trigonal-bipyramidal sites located in the Sr,Na-containing O layers [$M(3)$ sites].

DeRoy, Besse, Chevalier & Gasperin (1987) selected $P\bar{6}2c$ for NaV₆O₁₁ from three possible space groups, $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$, because only $P\bar{6}2c$ gave consistent Na—O distances. They concluded that the $M(1)$ cation is not at the special position (6g) but at a general position (12i) of $P\bar{6}2c$ with a site occupancy of $\frac{1}{2}$, because the R value decreased from 0.065 to 0.036. Also in this study, these three space groups were compared by refining the structure in each of them using 1922 unaveraged intensities [$I > 1.5\sigma(I)$]: $P6_3/mmc$, $R = 0.020$ and $wR = 0.036$ with 26 parameters; $P\bar{6}2c$ (model A, 6g), $R = 0.0189$ and $wR = 0.03497$ with 32 parameters; $P\bar{6}2c$ (model A, 12i), $R = 0.0187$ and $wR = 0.03467$ with 36 parameters; $P\bar{6}2c$ (model B, 6g), $R = 0.0190$ and $wR = 0.03500$ with 32 parameters; $P\bar{6}2c$ (model B, 12i), $R = 0.0186$ and $wR = 0.03462$ with 36 parameters; $P6_3mc$ (model C), $R = 0.0187$ and $wR = 0.0329$ with 43 parameters; and $P6_3mc$ (model D), $R = 0.0186$ and $wR = 0.0331$ with 43 parameters. The 12i models in $P\bar{6}2c$ were not followed up because

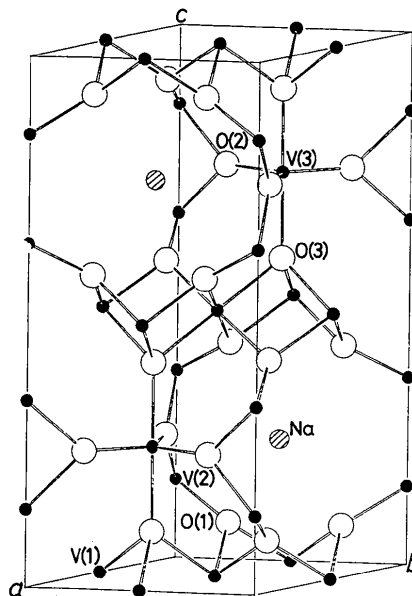


Fig. 1. Unit cell of the structure of NaV₆O₁₁. Shaded circles represent Na, solid circles V, and open circles O atoms. The V(n) sites correspond to the $M(n)$ sites of BaTi₂Fe₄O₁₁, BaSn₂Fe₄O₁₁ and BaFe₁₂O₁₉ ($n = 1-3$); the $M(3)$ sites of these three compounds are slightly split along [001].

they did not decrease R and wR significantly. Though R and wR values of any of the models are lower than those of the $P6_3/mmc$ model, the differences are too small to be significant. The differences of R or wR within each pair of models are also very small, and there are no correlations between $|F_o(hkl)| - |F_o(\bar{h}\bar{k}\bar{l})|$ and $|F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})|$ for more than 50 selected Bijvoet pairs with large Q values: $Q = 2[|F_c(hkl)|^2 - |F_c(\bar{h}\bar{k}\bar{l})|^2]/[|F_c(hkl)|^2 + |F_c(\bar{h}\bar{k}\bar{l})|^2]$. From these three space groups, $P6_3/mmc$ has therefore been selected for $\text{NaV}_6\text{O}_{11}$; the Na—O distances of the refined model are consistent with $r(\text{XII Na}^+) + r(\text{IV O}^{2-}) = 2.77 \text{ \AA}$ (Shannon, 1976).

The structure of $\text{SrV}_6\text{O}_{11}$ was refined in three possible space groups, $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$ using 2031 unaveraged intensities [$I > 3\sigma(I)$]: $P6_3/mmc$, $R = 0.070$ with 24 parameters; $P\bar{6}2c$, $R = 0.069$ with 24 parameters; and $P6_3mc$, $R = 0.064$ with 35 parameters. In all three models, the anisotropic thermal parameters of O(2) could not be refined successfully [$U(2,2) < 0$]. Further difficulties arose in refining the anisotropic thermal parameters of other atoms in the last two models. If we take the different numbers of parameters into account, the differences between the R values are indeed small and probably insignificant. We prefer the highest symmetry, $P6_3/mmc$.

In $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$, $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaFe}_{12}\text{O}_{19}$ (Townes, Fang & Perrotta, 1967; Cadée & Ijdo, 1984), the $M(3)$ sites (trigonal-bipyramidal sites) are occupied exclusively by Fe atoms, and split along [001] into pairs of distorted tetrahedral sites. The present study also refined structure parameters of $\text{SrV}_6\text{O}_{11}$ and $\text{NaV}_6\text{O}_{11}$ with their V(3) sites split. The refinements gave the V(3)—V(3^{iv}) splitting distances, $\text{SrV}_6\text{O}_{11} = 0.231(8)$ and $\text{NaV}_6\text{O}_{11} = 0.132(1) \text{ \AA}$, which are relatively small compared to those of the others (Table 2). The R factors changed very little: $\text{SrV}_6\text{O}_{11}$ from 6.049 to 6.038% and $\text{NaV}_6\text{O}_{11}$ from 1.684 to 1.678%. We conclude that the V(3) sites of $\text{SrV}_6\text{O}_{11}$ and $\text{NaV}_6\text{O}_{11}$ are not split. This conclusion is consistent with the general tendency that Fe^{3+} can also occupy a four-coordinated site while neither V^{3+} nor V^{4+} takes a fourfold coordination.

The cell constant c varies widely among $\text{SrV}_6\text{O}_{11}$, $\text{NaV}_6\text{O}_{11}$, $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$, and appears to be strongly correlated with the splitting of the $M(3)$ site. Indeed, the difference in c dimensions between any two compounds is roughly equal to that in the $M(3)$ — $M(3^{\text{iv}})$ distances. The splitting gives rise to two different axial $M(3)$ —O distances. The shorter $M(3)$ —O(3^{iii,iv}) distance is maintained almost constant among the four compounds while the longer one varies with the splitting distance of the $M(3)$ site (Table 2). The $M(2)$ — $M(2^{\text{v}})$ distance is also correlated with the splitting of the $M(3)$ site. The difference in the $M(2)$ — $M(2^{\text{v}})$ distances between any

Table 3. *Electrostatically most stable charge distributions among $M(1)$, $M(2)$ and $M(3)$ sites, electrostatic potentials, φ (e \AA^{-1}), at $M(1)$, $M(2)$ and $M(3)$ sites, and Madelung energies, ΔE (MJ mol^{-1}), of $\text{SrV}_6\text{O}_{11}$, $\text{NaV}_6\text{O}_{11}$, $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$*

	$\text{NaV}_6\text{O}_{11}$	$\text{SrV}_6\text{O}_{11}$	$\text{BaTi}_2\text{Fe}_4\text{O}_{11}^*$	$\text{BaSn}_2\text{Fe}_4\text{O}_{11}^*$
$M(1)$	+3	+3	+3	+3
$M(2a)$	+4	+4	+4	+4
$M(2b)$	+4	+4	+4	+4
$M(3)$	+4	+3	+3	+3
$\varphi[M(1)]$	-2.502	-2.501	-2.482	-2.443
$\varphi[M(2a)]$	-3.041	-2.983	-2.946	-2.838
$\varphi[M(2b)]$	-3.041	-2.983	-3.020	-2.919
$\varphi[M(3)]$	-3.085	-2.563	-2.413	-2.413
ΔE	-5.743	-5.492	-5.415	-5.305

* The $M(3)$ sites are split along [001] into two sites. Metal ions are situated in one of the split sites at random. For the calculations, however, the metal ions were supposed to occupy one of the two sites according to the symmetry $P6_3mc$. Consequently, the $M(2)$ site which is closer to the neighboring occupied $M(3)$ site, $M(2a)$, and the remaining one, $M(2b)$, are not equivalent.

two compounds is about half of that in the $M(3)$ — $M(3^{\text{iv}})$ distance. That is, among the four compounds, the differences in the cell parameters c and the $M(2)$ — $M(2^{\text{v}})$ distances are almost attributed to the splitting of the $M(3)$ sites, and the structure of the unit composed by an $M(1)$ —O(1), O(3) octahedra layer perpendicular to [001] and two adjacent $M(2)$ layers is essentially unchanged.

Madelung energies were calculated by the Fourier method on $\text{SrV}_6\text{O}_{11}$, $\text{NaV}_6\text{O}_{11}$, $\text{BaTi}_2\text{Fe}_4\text{O}_{11}$ and $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$, for several valence combinations of $M(1)$, $M(2)$ and $M(3)$ sites. The results, listed in Table 3, suggest that $M(1)$ sites are favored by trivalent cations while $M(2)$ sites by tetravalent cations in every compound, and that the $M(3)$ site is preferred by a tetravalent cation in $\text{NaV}_6\text{O}_{11}$ while it is preferred by trivalent cations in the remaining three compounds (Table 3). The bond-valence calculations (Brown & Altermatt, 1985) based on such cation distributions give reasonable valences of O ions [$\text{SrV}_6\text{O}_{11}$, O(1) = -2.01, O(2) = -1.95, O(3) = -1.76; $\text{NaV}_6\text{O}_{11}$, O(1) = -1.98, O(2) = -2.10, O(3) = -1.81]. These results together with those of Madelung energy calculations suggest that the $M(3)$ sites of the $AT_6\text{O}_{11}$ -type compounds are preferred by trivalent cations in the case of a divalent A ion and by tetravalent cations in the case of a monovalent A ion.

The Madelung energy calculations further suggest that tetravalent cations prefer the $M(2)$ sites to the $M(1)$ sites in the four compounds mentioned above. Indeed, in $\text{BaSn}_2\text{Fe}_4\text{O}_{11}$, the mean $M(1)$ —O distance, 2.024 \AA , agrees with $r(\text{VI Fe}^{3+}) + r(\text{IV O}^{2-}) = 2.025 \text{ \AA}$, and the mean $M(2)$ —O distance, 2.081 \AA , with $r(\text{VI Sn}^{4+}) + r(\text{IV O}^{2-}) = 2.07 \text{ \AA}$ (Shannon, 1976). In the other three compounds, however, the mean $M(1)$ —O distance and the mean $M(2)$ —O distance are almost equal, and are between the calculated

distances $r(\text{VI}M^{3+}) + r(\text{IV}O^{2-}) = 2.02 \text{ \AA}$ (SrV₆O₁₁ and NaV₆O₁₁), 2.025 \AA (BaTi₂Fe₄O₁₁) and $r(\text{VI}M^{4+}) + r(\text{IV}O^{2-}) = 1.96 \text{ \AA}$ (SrV₆O₁₁ and NaV₆O₁₁), 1.985 \AA (BaTi₂Fe₄O₁₁) (Shannon, 1976). In SrT_xV_{6-x}O₁₁ (T = Ti, Cr and Fe) compounds, the distribution of trivalent and tetravalent cations among the M(1), M(2) and M(3) sites does not always conform to the results of the Madelung energy calculations (Kanke, Izumi, Takayama-Muromachi, Kato, Kamiyama & Asano, 1990). A localized *d*-electron model cannot explain the spontaneous magnetization of magnetically ordered NaV₆O₁₁ (Uchida, Kanke, Takayama-Muromachi & Kato, 1991); besides, NaV₆O₁₁ is a good metallic conductor independent of its magnetic transition (Kanke, Takayama-Muromachi, Kato & Matsui, 1990; Uchida *et al.*, 1991). Further study is needed to reveal the electronic and magnetic structures of the AT₆O₁₁-type compounds.

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Structure of Sr₂Bi₂O₅ from X-ray and Neutron Powder Diffraction Data

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Abstract. Bismuth strontium oxide, Sr₂Bi₂O₅, *M_r* = 673.20, orthorhombic, *Cmcm*, *T* = 295 K, *a* = 3.8268 (2), *b* = 14.3142 (6), *c* = 6.1724 (4) Å, *V* = 338.11 (2) Å³, *Z* = 2, *D_x* = 6.612 (1) Mg m⁻³. Rietveld refinement using neutron powder diffraction data [$\lambda = 2.57171$ (7) Å, *F*(000) = 120.26 fm, 55 contributing reflections] resulted in *R_{wp}* = 4.31%. Around Bi lie four O atoms at short distances, forming a tetrahedron, approximately. However, the occupation of two of these positions is mutually exclusive, *i.e.* the effective coordination is threefold. The resulting umbrella-like BiO₃ groups are, on average, linked in pairs. The SrO₆ prisms share edges along [001] giving sheets perpendicular to [010]. Bond distances and angles are consistent with related materials containing stereochemically active lone pairs.

Introduction. The binary compound Sr₂Bi₂O₅ is of interest because of its relationship to the superconducting compounds Sr₂Bi₂Ca_{*n*-1}Cu_{*n*}O_{2*n*+4+ δ} , studied by the Solid State Group of Leiden University (Groen, 1990). The *T_c* of Sr₂Bi₂Ca_{*n*-1}Cu_{*n*}O_{2*n*+4+ δ} is strongly related to the O content (Groen & De Leeuw, 1989). The structure of Sr₂Bi₂O₅ is reported here. Guillermo, Conflant, Boivin & Thomas (1978) described the system SrO–Bi₂O₃, Conflant & Boivin (1979) and recently Abbattista, Brisi, Mazza & Valini (1991) studied the SrO–Bi₂O₃–O₂ system, but no crystal structures were determined. Moreover, bismuth oxide materials are of interest for their high ionic conduction properties.

Experimental. Sr₂Bi₂O₅ was prepared from AR Sr(NO₃)₂ and Bi₂O₃ by heating appropriate mixtures