

Sodium scandium arsenate, $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$

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Nasicon-type trisodium discandium tris(arsenate), $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$, contains a polyhedral network of vertex-sharing octahedral ScO_6 and tetrahedral AsO_4 units [$d_{\text{av}}(\text{Sc}-\text{O}) = 2.089(2) \text{ \AA}$ and $d_{\text{av}}(\text{As}-\text{O}) = 1.672(2) \text{ \AA}$] encapsulating two types of Na^+ species. The sodium site occupancies are similar to those of the equivalent species in $\beta\text{-Na}_3\text{Sc}_2(\text{PO}_4)_3$.

Comment

Based on the present refinement, $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$ adopts a centrosymmetric rhombohedral Nasicon structure (Sljukic *et al.*, 1969; Masquelier *et al.*, 2000), as indicated earlier on the basis of X-ray powder data (Winand *et al.*, 1990). However, a superstructure or other symmetry reduction, perhaps associated with sodium cation ordering, cannot be completely ruled out.

The stretched octahedral Na1 position (Wyckoff site $6b$) with site symmetry $\bar{3}$ is fully occupied within experimental error. Its bond valence sum (BVS), calculated by the Brown (1996) formalism, of 0.98 is in good agreement with the expected value of 1.00. Na2 occupies Wyckoff site $18e$ (symmetry 2) with an occupancy of 0.626 (11). This site is usually described as eight-coordinate (Masquelier *et al.*, 2000) to framework O atoms. In the title compound, two of these links are exceptionally long ($d > 3.16 \text{ \AA}$) and the Na2 coordination could equally well be described as sixfold. Bond valence sums for Na2 indicate significant underbonding if either six-coordinate (BVS = 0.76) and eight-coordinate (BVS = 0.81) is assumed.

The overall sodium unit-cell content of 17.27 (12) based on the refinement is in adequate agreement with the value of 18 required for charge-balancing purposes. Other Nasicon phases show a similar apparent reduced cation content, which may be rationalized on the basis of the mobility of these species in the extra-framework channel system (de la Rochère *et al.*, 1983). The sodium content of 18 can be formally achieved by full occupancy of the Na1 ($6b$) site and two-thirds occupancy of the Na2 ($18e$) site (Susman *et al.*, 1983).

The site occupancies of the sodium cations in $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$ are similar to those of the equivalent species in β -

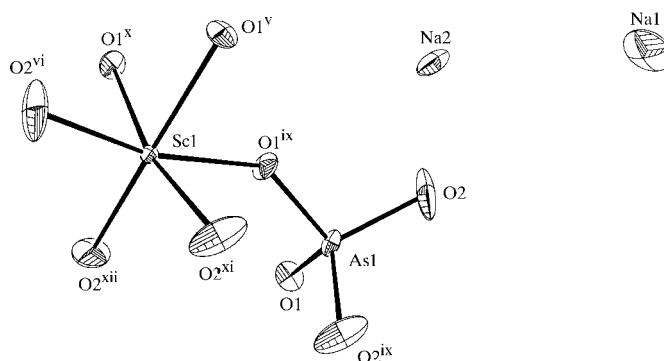


Figure 1

Fragment of the $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$ structure (50% displacement ellipsoids) showing the bonding environments of the Sc and As cations. [Symmetry codes: (v) $1+x-y, 1-y, \frac{1}{2}-z$; (vi) $\frac{1}{3}-x+y, \frac{2}{3}+y, z+\frac{1}{6}$; (ix) $-x, -x+y, \frac{1}{2}-z$; (x) $y, 1-x, \frac{1}{2}-z$; (xi) $\frac{1}{3}+x, \frac{2}{3}+x-y, z+\frac{1}{6}$; (xii) $\frac{1}{3}-y, \frac{2}{3}-x, z+\frac{1}{6}$.]

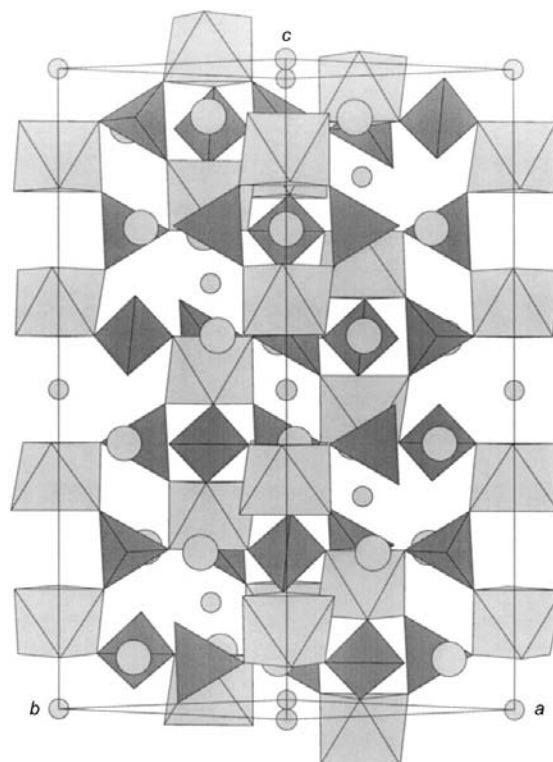


Figure 2

Polyhedral view down $[110]$ of the $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$ structure (ScO_6 octahedra are shown with light shading, AsO_4 tetrahedra with dark shading, Na1 as small circles and Na2 as large circles).

$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (Collin *et al.*, 1986), where the $6b$ and $18e$ Wyckoff sites are 0.92 (2) and 0.693 occupied, respectively (restrained total unit-cell sodium content = 17.99). At 473 K, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ shows a similar occupation pattern for the sodium cations, although this effect is strongly temperature dependent (de la Rochère *et al.*, 1983; Masquelier *et al.*, 2000).

The Sc1 atom adopts its usual octahedral coordination, with $d_{\text{av}}(\text{Sc}-\text{O}) = 2.089(2) \text{ \AA}$, and As1 is tetrahedral [$d_{\text{av}}(\text{As}-\text{O}) = 1.672(2) \text{ \AA}$]. The polyhedral linkage of the ScO_6 and AsO_4 moieties [$\theta_{\text{av}}(\text{Sc}-\text{O}-\text{As}) = 145.3^\circ$] to form the Nasicon framework has been described in detail elsewhere (Subramanian *et al.*, 1985; Masquelier *et al.*, 2000).

Experimental

Initially, Na₂CO₃ (4.01 g, 37.8 mmol, Aldrich), Sc₂O₃ (0.55 g, 4 mmol, Varlacoid) and (NH₄)H₂AsO₄ (8.58 g, 54 mmol; prepared by oxidizing As₂O₃ with H₂O₂ and titrating with NH₄OH) were heated in a Pt crucible at 1193 K for 16 h. Further Na₂CO₃ (4.01 g) and (NH₄)-H₂AsO₄ (8.58 g) were added and the mixture heated to 1193 K for another 24 h. The crucible was removed from the furnace and allowed to cool to ambient temperature, and was then returned to the 1193 K furnace for 4 h. The flux was decanted whilst hot and, upon cooling the crucible once more, the remaining solids were worked up in water. This resulted in a mixture of white powder and a few small single crystals of Na₃Sc₂(AsO₄)₃ (1.47 g; yield based on Sc = 64%).

Crystal data

Na ₃ Sc ₂ (AsO ₄) ₃	Mo K α radiation
$M_r = 575.64$	Cell parameters from 3531 reflections
Trigonal, $R\bar{3}c$	$\theta = 2.69\text{--}32.50^\circ$
$a = 9.2760(3) \text{ \AA}$	$\mu = 10.22 \text{ mm}^{-1}$
$c = 22.4640(8) \text{ \AA}$	$T = 298 \text{ K}$
$V = 1673.9 \text{ \AA}^3$	Rod, colourless
$Z = 6$	$0.05 \times 0.03 \times 0.03 \text{ mm}$
$D_x = 3.41 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART 1000 diffractometer	599 reflections with $I > \sigma(I)$
ω scans	$R_{\text{int}} = 0.054$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$\theta_{\text{max}} = 32.5^\circ$
$T_{\text{min}} = 0.536$, $T_{\text{max}} = 0.695$	$h = -14 \rightarrow 14$
16 306 measured reflections	$k = -14 \rightarrow 14$
673 independent reflections	$l = -33 \rightarrow 33$
	Intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.0004$
$R = 0.027$	$\Delta\rho_{\text{max}} = 1.14 \text{ e \AA}^{-3}$
$wR = 0.025$	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$
$S = 1.12$	Extinction correction: Larson (1967)
599 reflections	Extinction coefficient: 7 (2)
37 parameters	
Weighting: Chebyshev polynomial with 3 parameters (Carruthers & Watkin, 1979) 0.225, 0.116 and 0.141	

During data reduction, a handful of weak ($I < 1\%$ of I_{max}) reflections violating the R -centring condition were apparent. These could be accounted for by assuming a primitive trigonal cell of the same dimensions as that reported in the results section. However, no convincing model could be established in a primitive cell. The atomic parameters showed high correlations and oscillations when refined, suggesting that the primitive model symmetry was too low. Rhombohedral symmetry breaking and superstructure reflections have been seen in other Nasicons (d'Yvoire *et al.*, 1983). These have

Table 1

Selected geometric parameters (\AA , $^\circ$).

Na1—O1 ⁱ ($\times 6$)	2.4752 (18)	Sc1—O1 ^v ($\times 3$)	2.1303 (17)
Na2—O1 ⁱⁱ ($\times 2$)	2.539 (3)	Sc1—O2 ^{vi} ($\times 3$)	2.047 (2)
Na2—O1 ⁱⁱⁱ ($\times 2$)	2.552 (2)	As1—O1 ($\times 2$)	1.6755 (17)
Na2—O2 ($\times 2$)	2.624 (3)	As1—O2 ($\times 2$)	1.668 (2)
Na2—O2 ^{iv} ($\times 2$)	3.164 (3)		
Sc1 ^{viii} —O1—As1	139.4 (1)	Sc1 ^{viii} —O2—As1	151.2 (2)

Symmetry codes: (i) $\frac{1}{3} + x, y - \frac{1}{3}, z - \frac{1}{3}$; (ii) $\frac{2}{3} - y, \frac{1}{3} - x, z - \frac{1}{6}$; (iii) $-\frac{1}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iv) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{1}{3} - z$; (v) $1 + x - y, 1 - y, \frac{1}{2} - z$; (vi) $\frac{1}{3} - x + y, \frac{2}{3} + y, z + \frac{1}{6}$; (vii) $x - y, 1 - y, \frac{1}{2} - z$; (viii) $-\frac{1}{3} - x + y, y - \frac{2}{3}, z - \frac{1}{6}$.

tentatively been associated with an ordering of the extra-framework cations, although no detailed structural models to account for this behaviour have yet been developed. For the present refinement, the largest difference peak is 0.69 \AA from Na1.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SMART; program(s) used to refine structure: CRYSTALS (Watkin *et al.*, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and ATOMS (Shape Software, 1999); software used to prepare material for publication: CRYSTALS.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1304). Services for accessing these data are described at the back of the journal.

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