



Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

A sodium calcium arsenate, NaCa(AsO₄)Jinru Lin,^a Wei Sun,^b Jin-Xiao Mi^b and Yuanming Pan^{a*}^aDepartment of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada S7N 5E2, and ^bDepartment of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, Fujian Province, People's Republic of ChinaCorrespondence e-mail: yuanming.pan@usask.ca

Received 7 October 2011; accepted 24 October 2011

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{As}-\text{O}) = 0.002$ Å; R factor = 0.021; wR factor = 0.067; data-to-parameter ratio = 12.0.

The title compound, NaCa(AsO₄), was synthesized using a hydrothermal method at 633–643 K. It has a dense structure composed of alternating layers of distorted [CaO₆] octahedra and layers of [AsO₄] tetrahedra and distorted [NaO₆] octahedra, stacked along the a axis. The As, Ca and two O atoms lie on the mirror plane at $y = 1/4$ (*i.e.* $4c$), while the Na atom lies on an inversion centre ($1/2, 1/2, 0$) (*i.e.* $4b$). Each distorted [CaO₆] octahedron shares four equatorial common O vertices with four neighboring octahedra, forming a layer parallel to (100), whereas each distorted [NaO₆] octahedron shares two opposite edges with two neighboring ones, forming a chain running along [010]. Each isolated [AsO₄] tetrahedron shares two edges with two different [NaO₆] octahedra in one [NaO₆] chain and a vertex with another chain. Simultaneously the above [AsO₄] tetrahedron located in a four-membered [CaO₆] ring shares one edge of its base facet with one [CaO₆] octahedron and three corners with three other [CaO₆] octahedra of one [CaO₆] layer, and the remaining apex is shared with another [CaO₆] layer. [NaO₆] octahedra and [CaO₆] octahedra are linked to each other by sharing edges and vertices.

Related literature

For general background, see: Smedley & Kinniburgh (2002); Zhu *et al.* (2006); Rodríguez *et al.* (2008). For related structures, see: Graia *et al.* (1999) for CaNa₂(AsO₄)₃; IJdo (1982) for NaCa(VO₄); Ben Amara *et al.* (1983) for buchwaldite, NaCa(PO₄); Bredig (1942) for NaCa(PO₄).

Experimental

Crystal data

NaCa(AsO ₄)	$V = 400.97(15) \text{ \AA}^3$
$M_r = 201.99$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 11.486(2) \text{ \AA}$	$\mu = 9.73 \text{ mm}^{-1}$
$b = 6.6615(14) \text{ \AA}$	$T = 173 \text{ K}$
$c = 5.2406(11) \text{ \AA}$	$0.18 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	2163 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	505 independent reflections
$T_{\min} = 0.273, T_{\max} = 0.443$	498 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	42 parameters
$wR(F^2) = 0.067$	$\Delta\rho_{\max} = 0.83 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\min} = -0.74 \text{ e \AA}^{-3}$
505 reflections	

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2011) and ATOMS (Dowty, 2004); software used to prepare material for publication: SHELXL97.

This project was supported by the fund from the Natural Science and Engineering Research Council (NSERC) of Canada.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2179).

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supporting information

Acta Cryst. (2011). E67, i69 [https://doi.org/10.1107/S160053681104428X]

A sodium calcium arsenate, NaCa(AsO₄)

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S1. Comment

Arsenic, a highly toxic pollutant in surface and ground waters, poses serious health and environmental problems all around the world (Smedley & Kinniburgh, 2002). One common method for immobilization and remediation of arsenic contamination in aqueous environments is through co-precipitation with calcium by forming various Ca-arsenate compounds (Zhu *et al.*, 2006). To date, more than 20 Ca-arsenate compounds have been reported, but only a few of them have their crystal structures determined (Rodríguez *et al.*, 2008). Knowledge about the crystal structures of Ca-arsenate compounds is important for better understanding their stabilities and potential applications for remediation of arsenic contamination in aqueous environments. Herein we report on the hydrothermal synthesis and crystal structure of a new compound NaCa(AsO₄), which is the second sodium calcium arsenate after CaNa₂(AsO₄)₃ (Graia *et al.*, 1999).

The crystal structure of the title compound differs from those of its phosphorus and vanadium counterparts (Ijdo, 1982; Ben Amara *et al.*, 1983 & Bredig, 1942). The basic structural features of the title compound include [NaO₆] octahedra, [AsO₄] tetrahedra and [CaO₆] octahedra. Sodium atoms are surrounded by six O-atoms forming distorted [NaO₆] octahedra, which share edges to form chains running along [010] (Fig. 1–2). These octahedral chains are linked by isolated [AsO₄] tetrahedra to form polyhedral sheets parallel to the (100) plane (Fig. 2). This linkage is made by each [AsO₄] tetrahedron sharing edges with two [NaO₆] octahedra in one chain and a vertex with another chain. These sheets are then linked together by [CaO₆] octahedra *via* sharing edges and vertices (Fig. 1–3).

S2. Experimental

Single crystals of NaCa(AsO₄) were synthesized using a hydrothermal method. A mixture of 0.5 mmol calcium nitrate Ca(NO₃)₂·H₂O and 0.3 mmol sodium hydrogen arsenate heptahydrate Na₂HAsO₄·H₂O was added to 5 ml of 2M NaOH solution. This mixed solution was then transferred into a 22 ml pressure vessel from Parr Instrument Company and heated to and maintained at a temperature of 633–643 K for 13 days. Solid products were filtered, washed with deionized water, and dried in the air. Crystals with a rectangular morphology were selected with a polarizing microscope for the collection of single-crystal X-ray diffraction data at 173 K.

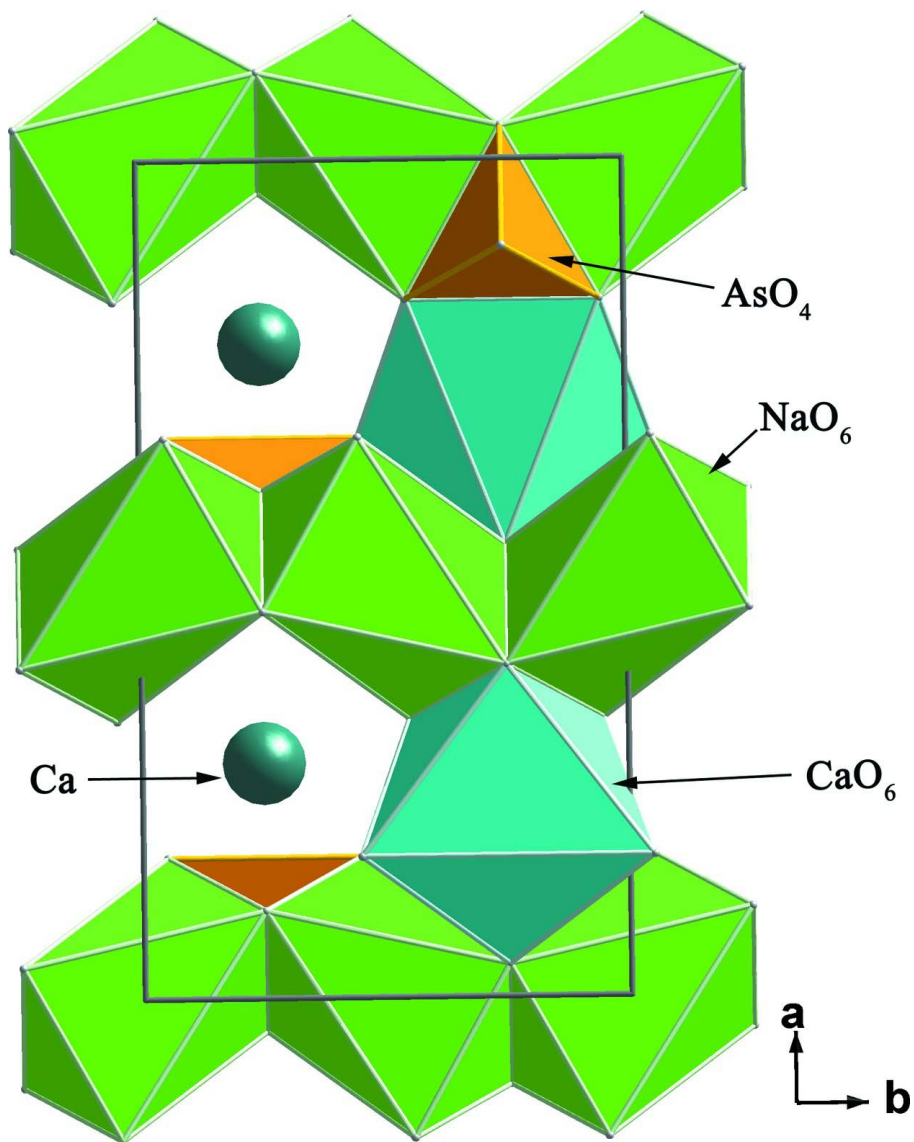


Figure 1
The crystal structure of NaCa(AsO₄) plotted in projection along [001].

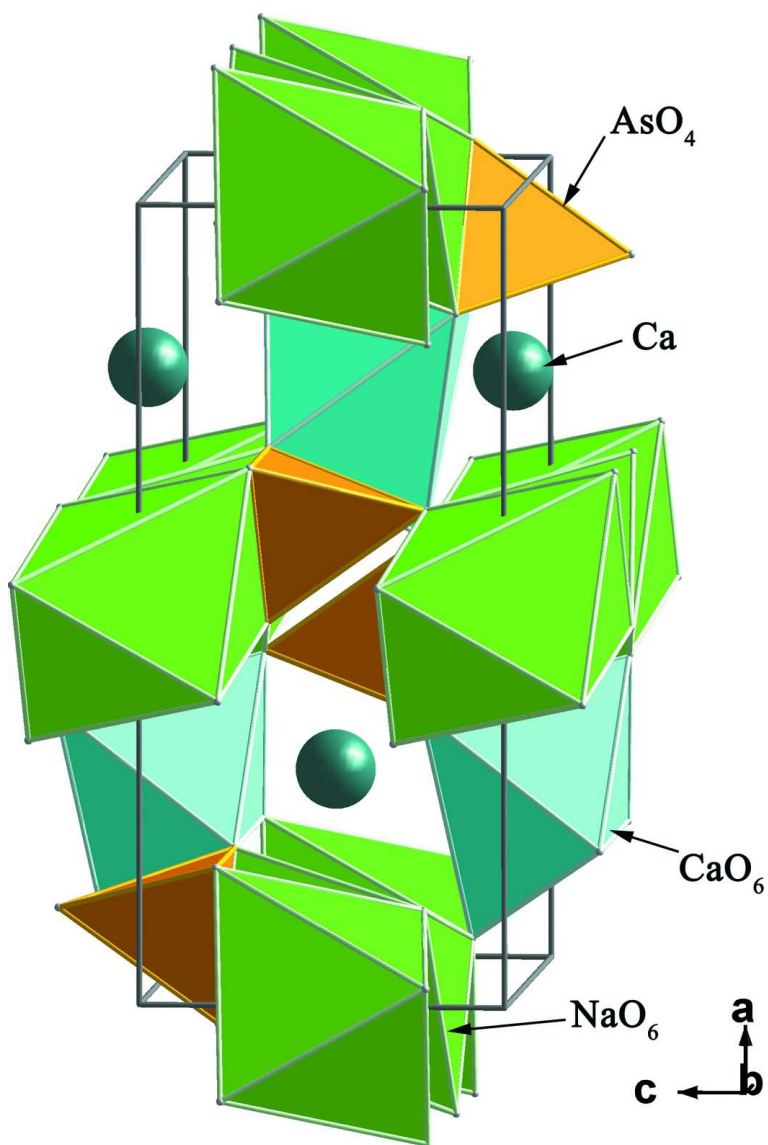


Figure 2

The crystal structure of NaCa(AsO₄) plotted in projection along a direction near [010].

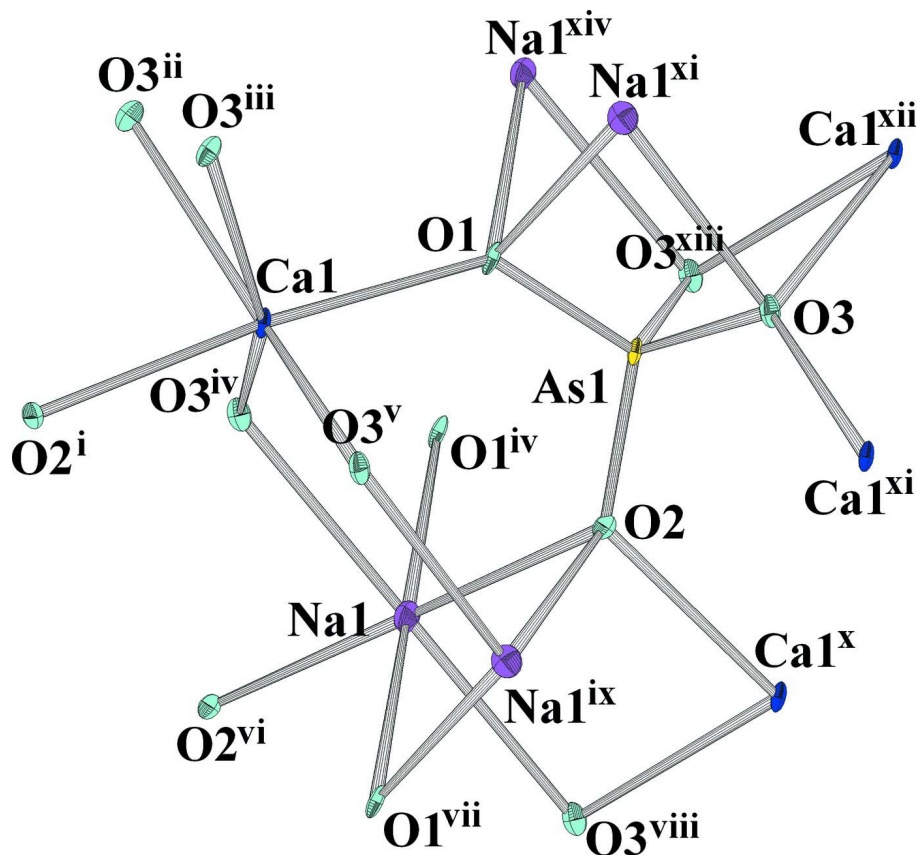


Figure 3

Coordination environment of Ca, Na, As and O atoms, with displacement ellipsoids drawn at the 50% probability level (symmetry codes: (i) $-0.5+x, 0.5-y, 0.5-z$; (ii) $-0.5+x, 0.5-y, 1.5-z$; (iii) $-0.5+x, y, 1.5-z$; (iv) $1-x, 0.5+y, 1-z$; (v) $1-x, -y, 1-z$; (vi) $1-x, 0.5+y, -z$; (vii) $x, y, -1+z$; (viii) $x, 0.5-y, -1+z$; (ix) $1-x, -0.5+y, -z$; (x) $0.5+x, 0.5-y, 0.5-z$; (xi) $1-x, -0.5+y, 1-z$; (xii) $0.5+x, 0.5-y, 1.5-z$; (xiii) $x, 0.5-y, z$; (xiv) $x, y, z+1$).

sodium calcium arsenate

Crystal data

NaCa(AsO₄)

$M_r = 201.99$

Orthorhombic, *Pnma*

Hall symbol: $-P\ 2ac\ 2n$

$a = 11.486\ (2)\ \text{\AA}$

$b = 6.6615\ (14)\ \text{\AA}$

$c = 5.2406\ (11)\ \text{\AA}$

$V = 400.97\ (15)\ \text{\AA}^3$

$Z = 4$

$F(000) = 384$

$D_x = 3.346\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2163 reflections

$\theta = 3.6\text{--}28.2^\circ$

$\mu = 9.73\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Prism, colorless

$0.18 \times 0.12 \times 0.10\ \text{mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

1200 images, $\Delta\omega = 1^\circ$, Exp time: 15 s. scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2001)

$T_{\min} = 0.273, T_{\max} = 0.443$

2163 measured reflections

505 independent reflections

498 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\text{max}} = 28.2^\circ$, $\theta_{\text{min}} = 3.6^\circ$

$h = -15 \rightarrow 14$
 $k = -5 \rightarrow 8$
 $l = -6 \rightarrow 6$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.067$
 $S = 1.03$
 505 reflections
 42 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 $w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.5926P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.83 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.74 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.017 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.59797 (3)	0.2500	0.56866 (7)	0.0046 (2)
Na1	0.5000	0.5000	0.0000	0.0088 (3)
Ca1	0.28059 (6)	0.2500	0.49344 (14)	0.0053 (2)
O1	0.4611 (2)	0.2500	0.6849 (5)	0.0075 (5)
O2	0.6038 (2)	0.2500	0.2482 (6)	0.0068 (6)
O3	0.66769 (14)	0.0513 (3)	0.7038 (3)	0.0068 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0014 (3)	0.0050 (3)	0.0073 (3)	0.000	0.00013 (11)	0.000
Na1	0.0076 (7)	0.0087 (7)	0.0101 (7)	0.0027 (6)	-0.0003 (6)	-0.0014 (6)
Ca1	0.0017 (4)	0.0051 (4)	0.0091 (4)	0.000	-0.0002 (2)	0.000
O1	0.0017 (10)	0.0096 (12)	0.0111 (12)	0.000	0.0023 (9)	0.000
O2	0.0042 (12)	0.0100 (13)	0.0062 (13)	0.000	0.0012 (8)	0.000
O3	0.0056 (8)	0.0048 (8)	0.0099 (8)	0.0014 (6)	-0.0024 (7)	0.0000 (7)

Geometric parameters (\AA , $^\circ$)

As1—O2	1.681 (3)	Na1—O3 ^v	2.4970 (18)
As1—O1	1.686 (2)	Na1—O3 ^{vi}	2.4970 (18)
As1—O3 ⁱ	1.7015 (17)	Ca1—O1	2.304 (3)

As1—O3	1.7015 (17)	Ca1—O3 ^{vi}	2.3346 (19)
Na1—O1 ⁱⁱ	2.3873 (19)	Ca1—O3 ^{vii}	2.3346 (19)
Na1—O1 ⁱⁱⁱ	2.3874 (19)	Ca1—O2 ^{viii}	2.393 (3)
Na1—O2	2.426 (2)	Ca1—O3 ^{ix}	2.4393 (19)
Na1—O2 ^{iv}	2.426 (2)	Ca1—O3 ^x	2.4393 (19)
O2—As1—O1	113.48 (12)	O2 ^{iv} —Na1—O3 ^{vi}	81.96 (8)
O2—As1—O3 ⁱ	113.41 (8)	O1—Ca1—O3 ^{vi}	87.93 (6)
O1—As1—O3 ⁱ	106.76 (8)	O1—Ca1—O3 ^{vii}	87.93 (6)
O2—As1—O3	113.41 (8)	O3 ^{vi} —Ca1—O3 ^{vii}	118.57 (10)
O1—As1—O3	106.76 (8)	O1—Ca1—O2 ^{viii}	173.87 (10)
O3 ⁱ —As1—O3	102.14 (12)	O3 ^{vi} —Ca1—O2 ^{viii}	88.94 (6)
O1 ⁱⁱ —Na1—O2	89.08 (7)	O3 ^{vii} —Ca1—O2 ^{viii}	88.94 (6)
O1 ⁱⁱⁱ —Na1—O2	90.92 (7)	O1—Ca1—O3 ^{ix}	101.26 (7)
O1 ⁱⁱ —Na1—O2 ^{iv}	90.92 (7)	O3 ^{vi} —Ca1—O3 ^{ix}	87.52 (4)
O1 ⁱⁱⁱ —Na1—O2 ^{iv}	89.08 (7)	O3 ^{vii} —Ca1—O3 ^{ix}	152.85 (7)
O1 ⁱⁱ —Na1—O3 ^v	67.60 (7)	O2 ^{viii} —Ca1—O3 ^{ix}	83.86 (7)
O1 ⁱⁱⁱ —Na1—O3 ^v	112.40 (7)	O1—Ca1—O3 ^x	101.26 (7)
O2—Na1—O3 ^v	81.96 (8)	O3 ^{vi} —Ca1—O3 ^x	152.85 (7)
O2 ^{iv} —Na1—O3 ^v	98.04 (8)	O3 ^{vii} —Ca1—O3 ^x	87.52 (4)
O1 ⁱⁱ —Na1—O3 ^{vi}	112.40 (7)	O2 ^{viii} —Ca1—O3 ^x	83.86 (7)
O1 ⁱⁱⁱ —Na1—O3 ^{vi}	67.60 (7)	O3 ^{ix} —Ca1—O3 ^x	65.72 (8)
O2—Na1—O3 ^{vi}	98.04 (8)		

Symmetry codes: (i) $x, -y+1/2, z$; (ii) $x, y, z-1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$; (v) $x, -y+1/2, z-1$; (vi) $-x+1, y+1/2, -z+1$; (vii) $-x+1, -y, -z+1$; (viii) $x-1/2, y, -z+1/2$; (ix) $x-1/2, -y+1/2, -z+3/2$; (x) $x-1/2, y, -z+3/2$.