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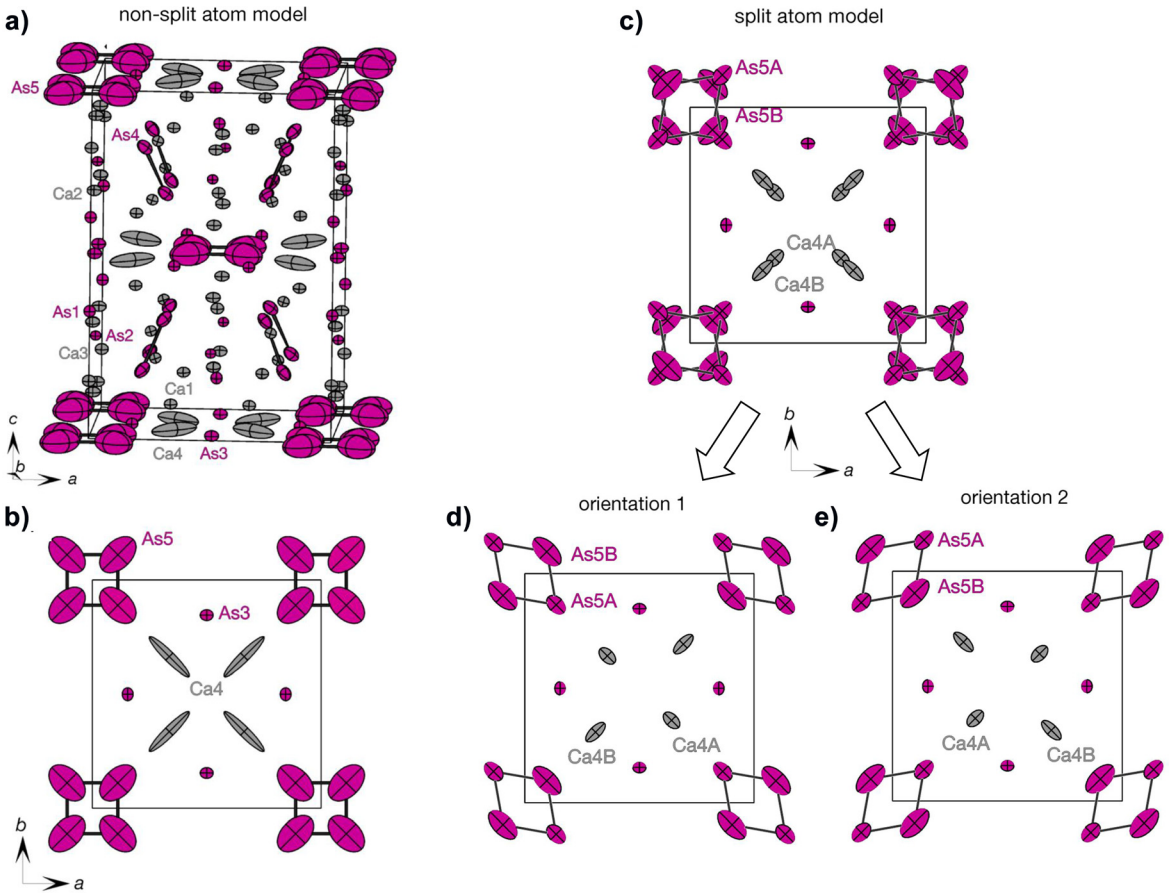
Crystal structure of undecacalcium decaarsenide, $Ca_{11}As_{10}$



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Abstract

$Ca_{11}As_{10}$, tetragonal, $I4/mmm$ (no. 139), a = 11.2532(1) Å, c = 16.2351(4) Å, and V = 2055.92(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0347, $wR_{ref}(F^2)$ = 0.0931, T = 150 K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Plate, dark grey
Size:	0.2 × 0.12 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	18.75 mm^{-1}
Diffractometer, scan mode:	Xcalibur, φ and ω-scans
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15,111, 722, 0.064
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 596
$N(param)_{refined}$:	49
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
As1	0.0000	0.0000	0.36542 (10)	0.0110 (4)
As2	0.0000	0.5000	0.2500	0.0083 (4)
As3	0.15420 (11)	0.5000	0.0000	0.0123 (3)
As4	0.20819 (6)	0.20819 (6)	0.18043 (6)	0.0178 (3)
As5A[a]	0.1369 (7)	0.1369 (7)	0.0000	0.095 (3)
As5B[b]	0.0948 (5)	0.0948 (5)	0.0000	0.067 (2)
Ca1	0.33766 (15)	0.0000	0.10361 (10)	0.0132 (4)
Ca2	0.25281 (15)	0.0000	0.31152 (10)	0.0121 (4)
Ca3	0.0000	0.0000	0.1657 (2)	0.0123 (7)
Ca4A[a]	0.3592 (7)	0.3592 (7)	0.0000	0.0218 (19)
Ca4B[b]	0.3077(9)	0.3077 (9)	0.0000	0.030 (2)

Occupanies: [a]0.506(16), [b]0.494(16).

Crystal structure of $Ca_{11}As_{10}$ (Ca – light gray and As – magenta): a) and b) non-split atom model; c)–e) split atom model. Atoms are represented as atomic displacement ellipsoids with 90% probability level. The covalent As–As bonds are shown in black.

Source of material

The title compound $Ca_{11}As_{10}$ has been synthesized via high-temperature solid-state reaction. Sample preparation and manipulations were done under protective atmosphere in an argon-filled glove box (MBraun 20G, argon purity 99.998%). Starting materials were elements of high purity: ingots of calcium (Alfa Aesar, 99.5%) and arsenic pieces (ChemPur, 99.999%). The compound $Ca_{11}As_{10}$ was prepared by placing Ca and As (11:10) in a graphitized silica ampoule and heat-treated in a Muffel furnace. The sealed ampoule was heated to 1173 K in 6 h, held at this temperature for 48 h and then cooled to 973 K in 42 h. After 24 h at 973 K the ampoule was cooled to room-temperature with a rate of 4.5 K/min.

Experimental details

The ampoule was opened in the glove box and capillaries (XRD capillaries, Hilgenberg, 0.3 mm inner diameter) were prepared for powder X-ray diffraction analysis. The product was investigated by means of powder X-ray diffraction (Stoe StadiP with Ge (111) monochromized Cu-$K_{\alpha 1}$ radiation (1.54056 Å)). An external Si standard was used for data correction. Single crystal X-ray diffraction was performed with an Oxford Diffractions Xcalibur 3 with graphite monochromatized Mo-K_α radiation (0.71071 Å) at 150 K. The sample is air and moisture sensitive. The powder X-ray diffraction pattern for the sample Ca–As (11:10) shows the binary phases $Ca_{11}As_{10}$ and CaAs. The tetragonal lattice parameters were obtained from least-square fits of the powder data using Rietveld refinement. Single crystal data for $Ca_{11}As_{10}$ were collected at 150 K under constant N_2-flow. An empirical absorption correction was applied [1]. The starting atomic parameters for $Ca_{11}As_{10}$ were deduced from an automatic interpretation of Direct Methods with SHELXS-97 [2]. The structures were then refined using SHELXL-97 (full-matrix least-square on F_O^2) [3] with anisotropic atomic displacement parameters for all atoms. The occupancy parameters for each atom were refined in separate least-squares cycles to check the correct composition of the title compound.

Discussion

So far, seven binary Ca–As compounds have been investigated: $CaAs_3$, Ca_2As_3, CaAs, $Ca_{16}As_{11}$, Ca_4As_3, Ca_5As_3 and Ca_2As [4–10]. All binary phases except Ca_5As_3 and Ca_2As, which are intermetallic compounds, belong to the Zintl phases with polyanionic substructures. The dimensionality of the polyanionic substructure decreases with increasing Ca-content. In $CaAs_3$ the As-substructure is made up by $[As_3]^{2-}$ networks, in Ca_2As_3 the As forms $[As_6]^{8-}$ chairs and in CaAs and $Ca_{16}As_{11}$ compounds the $[As–As]^{4-}$ dumbbells are present. In the structure of Zintl phase Ca_4As_3 both $[As–As]^{4-}$ dumbbells and isolated As^{3-} are found as polyanions.

The title compound $Ca_{11}As_{10}$ is the second (besides $Eu_{11}As_{10}$ [11]) As-representative of the $Ho_{11}Ge_{10}$ structure type [12]. The structure contains 8 $[As_2]^{4-}$ dumbbells, 2 tetrameric $[As_4]^{4-}$ units, 16 isolated As^{3-} anions and 44 Ca^{2+} cations and thus corresponds to an electron-precise Zintl phase. The disorder on the 8*h* position of As5 with rather large anisotropic displacement parameters is similarly present in other $Ho_{11}Ge_{10}$ – type representatives [13–16], and a reduction in symmetry to the orthorhombic *Immm* space group (as was applied for $Ba_{11}Sb_{10}$ [17]) does not solve the disorder problem. The crystal structure was therefore refined in the tetragonal *I*4/*mmm* space group but the 8*h* Wyckoff position of As5 and Ca4 were each split into two positions: As5A and As5B, Ca4A and Ca4B, respectively. The occupancy for Ca4A and Ca4B as well as for As5A and As5B was refined to 0.5 each. The distances between the As atoms in the dumbbell of 2.622(1) Å and in the $[As_4]^{4-}$ unit of 2.650(10) Å are slightly longer as in other binary Ca–As compounds. The distances between As

atoms and Ca atoms range from 2.718(13) Å to 3.538(11) Å within the first coordination sphere.

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