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Na_3As revisited: high-pressure synthesis of single crystals and structure refinement

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Abstract

Single crystals of Na_3As have been obtained from the elements by high-pressure–high-temperature reaction in a modified Belt-type apparatus. The compound crystallizes hexagonally, space group $P6_3cm$, with $a = 8.7838(8)$ Å, $c = 8.9990(12)$ Å, $c/a = 1.0245$ and $Z = 6$. The structure refinement ($R = 0.027$, $R_w = 0.017$ for 303 absorption-corrected unique reflections) shows unequivocally that Na_3As is isostructural with Cu_3P and that the structure models proposed by Brauer and Zintl (referred to as "Na_3As type" in the literature, space group $P6_3/mmc$) and Mansmann (anti-LaF_3 type, space group $P\bar{3}c1$) are wrong.

Keywords: High pressure synthesis; Structure refinement; Single crystals

1. Introduction

In a recent compilation [1], 35 compounds adopting the Na_3As structural type are listed. The list contains alkali metal pnictides (from Li_3P to Rb_3Bi) as well as intermetallic compounds (e.g. Mg_3Pt, Mg_3Au or Mg_3Hg) and hydrides (e.g. H_3Pu). With two exceptions (Al_3Ir [2] and Na_3Hg [3], see Discussion), however, the structure type assignments have been based solely on X-ray powder data.

The structure of the prototype compound Na_3As was derived in 1937 by Brauer and Zintl [4] from a Debye–Scherrer pattern (Cu Kα, 19 reflections) as hexagonal, space group $P6_3/mmc$, with $a = 5.088$ Å, $c = 8.982$ Å, $c/a = 1.7653$ and $Z = 2$.

Because the Na_3As type has been described [4] as nearly anti-isomorphic with the LaF_3 (tysonite) type, discussions with respect to the true unit cell size and space group of the latter have influenced the Na_3As discussion as well. Mansmann [5] found a triple hexagonal cell ($a' = 3^{1/2}a$, $c' = c$) and space group $P\bar{3}c1$ to be the correct one for LaF_3. By analogy, he suggested the same space group (and structure) for compounds like Mg_3Pt and, after a reinterpretation of the powder data published by Brauer and Zintl [4], Na_3As as well [6].

In two recent papers [7,8] we have shown for the intermetallic compounds Mg_3Au, Mg_3Pt and Mg_3Ir, which have been assumed to adopt the Na_3As structural type, that the triple hexagonal cell is indeed the correct one. There is no need to lower the Laue symmetry from hexagonal to trigonal; the space group, however, is not centric ($P6_3/mcm$), but acentric ($P6_3cm$). Mg_3Au, Mg_3Pt and Mg_3Ir are therefore isostructural with Cu_3P [9].

These results prompted us to reconsider the structure of Na_3As. Three main questions have to be answered in the course of a structure determination:

(i) Is the correct hexagonal unit cell of Na_3As the small one (a,c), as suggested by Brauer and Zintl [4], or the triple one ($a' = 3^{1/2}a$, $c' = c$)?

(ii) Is the correct Laue class $6/mmm$ or $\bar{3}m1$?

(iii) Is the correct space group centric or acentric? Evidently, single-crystal X-ray data are needed to solve the problem.

Unfortunately, during the preparation of Na_3As difficulties arise from the relatively high vapour pressures of sodium and arsenic. We have now succeeded in the preparation of Na_3As single crystals by synthesis in a closed high-pressure system. This method avoids the vaporization losses inevitably found in normal pressure experiments and allows for a rather exact control of composition even at the high temperatures which are needed for single-crystal growth. It has been successfully

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applied before for the synthesis of intermetallic phases in other systems with highly volatile components ([7], and references cited therein).

2. Experimental details

High-pressure experiments were carried out in a modified Belt-type apparatus [10] using capsules made from tantalum and starting with stoichiometric mixtures of sodium (t3N5; Alfa) and arsenic (m6N; Alfa). The elements as well as the capsules have been handled in a glove-box under carefully dried argon to avoid unwanted side reactions. Single crystals of Na_3As were formed after heating to 1000 °C at 15 kbar within 10 min, keeping the temperature at 1000 °C for 60 min, and subsequent quenching to ambient conditions. The homogeneous, brittle product contained dark-violet single crystals with well developed faces and edges. The crystal selected for the structure determination was fixed in a Lindemann glass capillary which then was sealed in the glove-box using an electrically heated platinum wire.

3. Structure analysis

A crystal with approximate dimensions $0.08 \times 0.08 \times 0.14$ mm^3 was checked by Weissenberg and oscillation photographs and subsequently used for data collection on an Enraf–Nonius CAD-4 diffractometer. Details of the structure analysis can be taken from Table 1.

Table 1
Crystallographic data and details of the crystal structure analysis for Na_3As

Space group	$P6_3cm$ (No. 185)
a (Å)	8.7838(8)
c (Å)	8.9990(12)
c/a	1.0245
V (Å^3)	601.3(1)
Z	6
Crystal size (mm^3)	$0.08 \times 0.08 \times 0.14$
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo Kα, $\lambda = 0.71069$ Å
Monochromator	Graphite
Scan mode, scan width (°)	$\omega/2\theta$, $0.75 + 0.35 \tan \theta$
Range of intensity measurement	$2° \leq \theta \leq 22.5°$
hkl limits	$-9 \leq h \leq 9$, $0 \leq k \leq 9$, $-9 \leq l \leq 9$
Intensities measured	1726
Absorption correction	DIFABS
Correction factors (max, min)	1.057, 0.934
Unique reflections, R_{int}	303, 0.017
Refined parameters, $(\Delta/\sigma)_{max}$	25, < 0.006
R, R_w	0.027, 0.017
$(\Delta\rho)_{max,min}$ (e Å^{-3})	+1.1, −0.8

From the X-ray film and diffractometer data the triple hexagonal unit cell with $a = 8.7838$ Å, $c = 8.9990$ Å, $c/a = 1.0245$ and $Z = 6$ was found to be the correct one for Na_3As. Therefore the smaller unit cell with space group $P6_3/mmc$ and hence the "Na_3As-type" structure proposed by Brauer and Zintl [4] can be excluded with certainty.

The only condition limiting possible reflections found was $l = 2n$ for $h\bar{h}0l$, pointing to a glide plane with component $c/2$ in $(11\bar{2}0)$ orientation. Merging of the 1726 collected intensities strongly suggested Laue class $6/mmm$ and therefore, according to the reflection conditions, $P6_3/mcm$ or $P6_3cm$ as possible space groups. In addition, space group $P\bar{3}cl$ was also included in the calculations in order to check Mansmann's proposal [6].

As in the case of Mg_3Pt [7], attempts to refine the structure showed immediately that the centric space groups $P6_3/mcm$ and $P\bar{3}cl$ are not appropriate for Na_3As (residuals after refinement in $P6_3/mcm$: $R = 0.074$, $R_w = 0.050$; after refinement in $P\bar{3}cl$: $R = 0.094$, $R_w = 0.057$; for details, see Ref. 11). A change to the acentric space group $P6_3cm$, however, immediately gave very satisfactory refinement results. The residuals dropped considerably and anisotropic refinement was possible without any problems.

At the end of the isotropic refinement a numerical correction for absorption was applied to the original 1726 data (programme DIFABS [12]; correction factors min. 0.934, max. 1.057; R_{int} after merging of the corrected data, 0.017) before performing the final anisotropic refinement. Final residuals were $R = 0.027$ and $R_w = 0.017$ ($w = 1/\sigma^2(F)$) for 25 refined parameters (including an extinction parameter) and 303 unique reflections (including unobserved ones). The maximum shift–error ratio in the final refinement cycle was less than 0.006; the maximum features in the final difference Fourier synthesis were +1.1 and −0.8 e Å^{-3}.

Atomic coordinates and equivalent isotropic displacement factors for Na_3As are given in Table 2 and derived interatomic distances in Table 3.

Table 2
Na_3As: atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^4$)

Atom	Position	x/a	y/b	z/c	U_{eq}[a]
As	$6c$ (..m)	0.3321(2)	0.3321(2)	0.75[b]	148(7)
Na(1)	$6c$ (..m)	0.3153(9)	0.3153(9)	0.0863(10)	596(47)
Na(2)	$6c$ (..m)	0.3518(6)	0.3518(6)	0.4231(7)	345(35)
Na(3)	$4b$ (3..)	1/3	2/3	0.2311(7)	262(21)
Na(4)	$2a$ (3.m)	0	0	0.2684(15)	929(76)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Fixed.

Table 3
Selected interatomic distances (Å) for Na_3As

As–Na(4)	2.922(2)	Na(1)–As	3.030(9)
As–Na(3)	2.938(2) (2×)	Na(1)–Na(2)	3.048(11)
As–Na(2)	2.947(6)	Na(1)–As	3.205(7) (2×)
As–Na(1)	3.030(9)	Na(1)–Na(4)	3.218(7)
As–Na(2)	3.184(5)	Na(1)–Na(2)	3.272(8)
As–Na(1)	3.205(7) (2×)	Na(1)–Na(3)	3.280(7) (2×)
As–Na(2)	3.387(5) (2×)	Na(1)–Na(2)	3.289(8) (2×)
As–Na(1)	3.430(7)	Na(1)–As	3.430(7)
		Na(1)–Na(4)	3.982(8)
Na(2)–As	2.947(6)		
Na(2)–Na(1)	3.048(11)	Na(3)–As	2.938(2) (3×)
Na(2)–As	3.184(5)	Na(3)–Na(1)	3.280(7) (3×)
Na(2)–Na(1)	3.272(8)	Na(3)–Na(2)	3.333(6) (3×)
Na(2)–Na(1)	3.289(8) (2×)	Na(3)–Na(2)	3.976(7) (3×)
Na(2)–Na(3)	3.333(6) (2×)		
Na(2)–As	3.387(5) (2×)	Na(4)–As	2.922(2) (3×)
Na(2)–Na(4)	3.389(5)	Na(4)–Na(1)	3.218(7) (3×)
Na(2)–Na(3)	3.976(7) (2×)	Na(4)–Na(2)	3.389(5) (3×)
		Na(4)–Na(1)	3.982(8) (3×)

4. Discussion

The results of the present single-crystal study show unequivocally that the triple hexagonal cell and the acentric space group $P6_3cm$ are indeed the correct ones for Na_3As. Therefore the structural models proposed by Brauer and Zintl (referred to as "Na_3As type" in the literature, space group $P6_3/mmc$, [4]) and Mansmann (anti-LaF_3 type, space group $P\bar{3}c1$, [6]) can be excluded with certainty.

Na_3As is isostructural with Cu_3P [9]. For a complete description of that structure the reader is referred to Olofsson's detailed discussion in Ref. [9].

Selected interatomic distances in Na_3As can be taken from Table 3. Arsenic is surrounded by 11 sodium atoms at distances ranging from 2.922 to 3.430 Å ($\langle As–Na \rangle = 3.143$ Å). The coordination numbers for Na(1) to Na(4) are 12 (4 As+8 Na), 13 (4 As+9 Na), 12 (3 As+9 Na) and 12 (3 As+9 Na), respectively.

For Cu_3P small deviations from the stoichiometric A_3X composition have been found [13–15]. The same is true for Mg_3Ir [8] and – to a lesser extent – for Mg_3Pt. We therefore refined the site occupancy factors (SOFs) for the single crystal of Na_3As used to get some information about its composition. The SOF for As was kept constant while the others were allowed to vary. The refinement resulted in SOFs for Na(1) to Na(4) which are close to their theoretical values within one to two standard deviations. This result is in agreement with the expectation that Na_3As as a valence compound should not exhibit any detectable range of homogeneity. It was further supported by the fact that the lattice constants for a second Na_3As crystal isolated from another high-pressure experiment agreed with the values for the first crystal within one standard deviation.

An interesting question is, of course, whether the results obtained for Na_3As can be generalized for other compounds that have been assumed to adopt the "Na_3As" structural type. For obvious reasons, we will restrict the following discussion to the first two classes of compounds mentioned in the introduction, namely the alkali metal pnictides and the intermetallic phases.

As far as the alkali metal pnictides are concerned, it has already been pointed out that the structure type assignments have been based solely on X-ray powder data. In the case of Na_3As itself, the powder reflections pointing to the triple hexagonal cell are rather weak (Table 4). Keeping in the mind the poor resolution of the Debye–Scherrer patterns used in the previous investigations, it is therefore not surprising that the weak superstructure reflections could simply not have been detected. Although the idea that the other alkali metal pnictides adopt the same acentric structure as Na_3As is certainly a very promising one, the question of the true unit cell size and symmetry of these compounds remains unsolved unless single-crystal data are available.

Concerning the A_3X intermetallic compounds, we have shown that Mg_3Au, Mg_3Pt and Mg_3Ir adopt the Cu_3P structural type [7,8]. Here again, most of the other compounds are characterized by X-ray powder patterns only. Two exceptions must be mentioned. The first one is Al_3Ir. Edshammar [2] assigned the "Na_3As"

Table 4
Comparison of the calculated X-ray powder patterns for Na_3As in two different structural models

	Model I[a] $P6_3cm$ $a = 8.7838$ Å $c = 8.9990$ Å		Model II[b] $P6_3/mmc$ $a' = 5.0713$ Å $(= a/3^{1/2})$ $c' = 8.9990$ Å $(= c)$	
2θ(°)[c]	*hkl*	$I_{calc.}$	*hkl*	$I_{calc.}$
19.714	002	46.4	002	43.5
20.202	110	33.5	100	30.8
22.508	111	73.6	101	62.1
28.374	112	0.2	–	–
30.755	202	1.3	–	–
32.669	211	1.2	–	–
35.369	300	100.0	110	100.0
36.235	113	99.1	103	96.1
37.076	212	0.4	–	–
40.044	004	6.3	004	5.5
40.815	302	34.5	112	30.5
41.069	220	4.0	200	3.8
41.837	104	0.5	–	–
42.331	221	12.4	201	9.0
44.048	311	0.4	–	–
45.249	114	0.4	–	–
45.949	222	0.2	–	–
51.535	223	25.4	203	26.2

[a] Calculated using the single-crystal data from Table 2.

[b] Calculated for the structural model given by Brauer and Zintl [4].

[c] For Cu Kα1 radiation (λ = 1.54056 Å).

type to this compound using Weissenberg photographs made with Cu Kα radiation. He derived the atomic coordinates from visually estimated intensities of the ($h0l$)-series. However, because no standard deviations and – even more important – no displacement parameters are given in his paper, it is difficult to estimate the reliability and accuracy of his structure determination.

The second exception is Na_3Hg, for which a structure determination based on single-crystal data has recently been published [3]. The authors refined the structure assuming a Na_3As-type structure according to Brauer and Zintl, i.e. using the small hexagonal unit cell and space group $P6_3/mmc$. They observed "abnormal" values for some of the displacement factors after the final refinement cycle, which are in their opinion, "physically senseless". We feel that this statement is not justified. To the contrary, refined displacement parameters have always a physical significance, because they are directly derived from observed quantities. If "abnormal" values are not merely due to a poor-quality data set (e.g. due to absent or insufficient correction for absorption), they will reflect some peculiarities of the structural model. One reason is frequently the presence of static displacements due to a wrong choice of the unit cell or the space group. We have found the same "irregular" behaviour of the displacement parameters in our early attempts to refine the structure of Mg_3Pt in a (wrong) centric space group [7]. After the change to the correct acentric space group the displacement factors became immediately "normal". A redetermination of the crystal structure of Na_3Hg therefore seems desirable.

Up to now, the only compound for which the small hexagonal unit cell and space group $P6_3/mmc$ have been confirmed by an accurate structure determination based on single-crystal X-ray data is Mg_2SiPt, which crystallizes in an ordered ternary variant of the "Na_3As structure" [16]. In this case the refinement was straightforward regarding convergence, displacement factors and residuals. Considering the fact that for all binary compounds of the "Na_3As family" carefully studied so far (Mg_3Au, Mg_3Pt, Mg_3Ir, Na_3As), the Cu_3P-type structure has been confirmed (see also Cd_3Au [17]), this result could mean that the Na_3As-type structure according to Brauer and Zintl is in fact a structural type more suited to ternary compounds, allowing for constituent atoms of rather different sizes. To verify this hypothesis, we plan the single-crystal synthesis and structure refinement of other ternary compounds, assumed to be members of the "Na_3As family". Candidates for such a study are compounds like the hitherto unknown Mg_2SiAu as well as compounds with an "inverse" composition, like $AlHfPt_2$ or $AlZrPt_2$ [18].

Finally, it should be noted that the displacement factors for Na(1) and Na(4) in Na_3As are larger than the corresponding ones for Na(2) and Na(3) by a factor of two to three. All attempts to refine Na(1) and Na(4) in split positions, however, have been unsuccessful. We believe therefore that these higher values are not due to static displacements but rather reflect the dynamics of the structure and might well be indicative of an approached phase transition at higher temperatures. Temperature-dependent single-crystal investigations to clarify the situation are in progress.

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