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Non-stoichiometric nickel arsenides in nature: The structure of orcelite, $Ni_{5-x}As_2$ ($x = 0.25$), from the Bon Accord oxide body, South Africa

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ABSTRACT

The crystal structure of the mineral orcelite, a rare nickel arsenide reported in the literature with the formula $Ni_{5-x}As_2$ (with $x = 0.23$), was refined using intensity data collected from a crystal from the Bon Accord body, South Africa. This study revealed that the structure is hexagonal, space group $P6_3mc$, with $a = 6.7922(2)$, $c = 12.4975(5)$ Å, and $V = 499.31(3)$ Å^3. The refinement of an anisotropic model led to an R index of 0.028 for 412 independent reflections. The orcelite structure can be described as a distorted variant of the Pd_5Sb_2 structure. The smaller As atoms are in the centres of distorted tetragonal antiprisms, formed by only Ni atoms. The coordination sphere is completed with two additional Ni atoms opposite to the rectangular faces. Electron microprobe data carried out on the same crystal used for the structural study point to the following formula [on the basis of $\Sigma(As + Fe + Sb)=2$]: $Ni_{4.75}(As_{1.93}Fe_{0.05}Sb_{0.02})$. According to the high-quality structure refinement, the minor elements were found to replace As in the structure. An atomic position for Ni was found to be partially occupied (75%), thus confirming the non-stoichiometry for the mineral orcelite previously reported in literature. Such a deviation from the stoichiometry could represent the driving force favouring disorder phenomena during the growth of the mineral.

1. Introduction

Six compounds belonging to the binary system Ni–As occur in nature: the three polymorphs of $NiAs_2$ (krutovite, rammelsbergite and pararammelsbergite), NiAs (nickeline), $Ni_{11}As_8$ (maucherite) and $Ni_{5-x}As_2$ (orcelite). These minerals correspond to the four known synthetic binary phases in the Ni–As system [1]. Among them, orcelite was originally described by Caillère et al. [2,3] from peridotitic rocks of the Tiebaghi massif, New Caledonia. Its occurrence, intimately intergrown with the mineral antigorite, allowed only to collect the X-ray powder diffraction pattern but precluded any approach to determine the crystal structure. Similar results were later obtained by Oen et al. [4] and Lorand and Pinet [5]. Nevertheless, a careful comparison of the powder pattern obtained for orcelite with that of the synthetic material [6] with formula $Ni_{5-x}As_2$ ($0.00 < x < 0.38$), showed a very good agreement except that the spacings for orcelite were smaller (0.02–0.05 Å). The best match was found with the powder pattern corresponding to synthetic $Ni_{4.77}As_2$. Notwithstanding, there were inconsistencies between the natural and synthetic compound, mainly related to the discrepancy involving the measured (8.55 g/cm^3) and calculated (8.50 g/cm^3) density of the mineral [7] and the eventual role played by the minor elements substituting for Ni and As (e.g., Sb, Cu, Fe and S). In the seventies, the crystal structure of synthetic Ni_5As_2 was independently studied by El-Boragy et al. [8] and Kjekshus [9] using three dimensional Weissenberg data. Although these Authors did no report high-quality diffraction data (R value = 0.095 in Ref. [9]), the structure was found to be hexagonal, space group $P6_3cm$, with $a = 6.815$ and $c = 12.506$ Å [9], and assigned to the Pd_5Sb_2-structure type. Finally, Oryshchyn et al. [10] recently re-determined the structure of pure synthetic Ni_5As_2 by means of single-crystal X-ray diffraction.

To help resolve the structural and chemical concerns relating to the mineral orcelite, we selected a grain coming from the Bon Accord oxide body, which is located in the north-western sector of the Barberton greenstone belt of South Africa. The mineralization consisted of a small semi-circular body associated with a serpentinite. One of the peculiarity of the Bon Accord oxide body is its extremely high enrichment in Ni (NiO values for the whole rock are >35%) [11]. Consistent with this geochemical data, the following six Ni-dominated minerals have been discovered at

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Bon Accord: bonaccordite, liebenbergite, "nichromite", nimite, trevorite and willemseite [12,13]. The entire body was removed in the 1920s, leaving a hole of about 6 m^3 in size [12]. Since the material was too refractory to smelt, the ore was discarded as a disordered pile about 3 km far from the original outcrop location. Later, the ore pile was completely removed and only a few hand specimens now are available for investigation.

Here we present new X-ray single-crystal and electron microprobe data for orcelite from the Bon Accord oxide body, South Africa.

2. Experimental

2.1. Single-crystal X-ray diffraction

In the investigated rock sample, orcelite occurs mainly associated with trevorite and only occasionally in contact with nepouite, willemseite and liebenbergite. It generally forms small grains (<20 μm in size) and only few grains reach a size of about 60 μm. A small crystal fragment (0.045 × 0.060 × 0.065 mm) was handpicked from the polished section given in Fig. 1. The crystal was preliminarily examined with a Bruker–Enraf MACH3 single-crystal diffractometer using graphite-monochromatized Mo Kα radiation. The data collection was then done with an Oxford Diffraction Xcalibur 3 diffractometer (X-ray Mo Kα radiation, λ = 0.71073 Å) fitted with a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarization corrections were done with the *CrysAlis* RED [14] software package. The program ABSPACK of the *CrysAlis* RED package [14] was used for the absorption correction. The merging R for the ψ-scan data set decreased from 0.076 before absorption correction to 0.032 after this correction. Reflections conditions ($h-k0l$: $l = 2n$; $000l$: $l = 2n$) were consistent with the space group $P6_3mc$ reported for synthetic Ni_5As_2 [8–10], and the statistical tests on the distribution of $|E|$ values strongly indicated the absence of an inversion centre ($|E^2-1| = 0.748$). The structure solution was then initiated in the space group $P6_3mc$.

The position of most of the atoms was determined from the three-dimensional Patterson synthesis [15]. A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an R factor of 10.12%. Three-dimensional difference Fourier synthesis yielded the position of the remaining two Ni atoms. The full-matrix least-squares program SHELXL-97 [15] was used for the refinement of the structure. Site-scattering values were refined using scattering curves for neutral species [16] as follows: Ni vs. [] (structural vacancy) and As vs. [] for the Ni and As sites, respectively. The Ni sites were found fully occupied except the Ni_6 position which was found to be partially occupied (75%). The mean electron number refined at the As_1 site (34.1 e^-) indicated the presence of a heavier element than As at the site (i.e., Sb), whereas the mean electron number at the As_3 site (32.6 e^-) indicated the presence of a lighter element (Fe) than As. As_2 was found to be fully occupied by As. At the last stage, with anisotropic atomic displacement parameters for all atoms and no constraints, the residual value settled at R = 0.027 (Rw = 0.054) for 365 independent observed reflections [$2\sigma(I)$ level] and 45 parameters and at R = 0.028 (Rw = 0.055) for all 412 independent reflections. Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 2.50 and 0.58 $e^-/Å^3$, respectively.

Experimental details and R indices are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are reported in Table 2 and anisotropic-displacement parameters in Table 3. Structure factors are available from the Authors upon request.

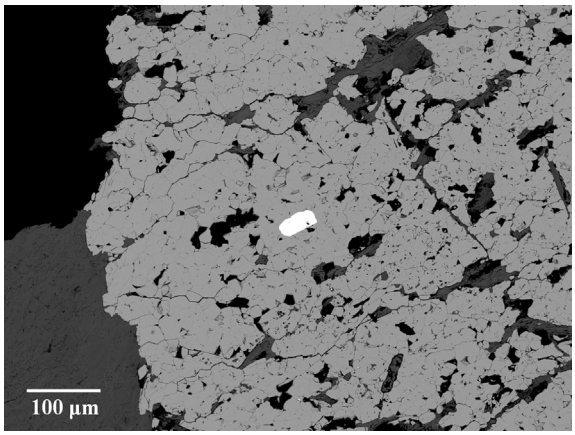

Fig. 1. SEM-BSE image of orcelite from Bon Accord (white grain) included in trevorite (light grey). The dark grey minerals are nepuoite and willemseite and the dark spots are holes and cracks of the polished section.

Table 1
Crystallographic data and refinement parameters for the selected orcelite crystal.

Crystal data	
Ideal formula	$Ni_{5-x}As_2$ (with x = 0.25)
Crystal system	hexagonal
Space group	$P6_3mc$
Unit-cell parameters (Å)	a = 6.7922(2), c = 12.4975(5)
Unit-cell volume (Å^3)	499.31(3)
Z	6
Crystal size (mm)	0.045 × 0.060 × 0.065
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3
Temperature (K)	298(3)
Radiation, wavelength (Å)	Mo Kα 0.71073
2θ max for data collection (°)	54.02
Crystal-detector dist. (mm)	50
h, k, l ranges	−8 to 8, −8 to 8, −15 to 14
Axis, frames, width (°), time per frame (s)	ω, 688, 1.00, 110
Total reflections collected	4325
Unique reflections (R_{int})	412 (0.032)
Unique reflections $I > 2\sigma(I)$	365
Data completeness to θ_{max} (%)	99.8
Absorption correction method	ABSPACK [14]
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	412/0/43
Flack parameter	0.10(5)
R_1 [$I > 2\sigma(I)$], wR_2 [$I > 2\sigma(I)$]	0.027, 0.054
R_1 all, wR_2 all	0.028, 0.055
Goodness-of-fit on F^2	1.531
Largest diff. peak and hole (e^-/Å^3)	2.50, −0.58

$$R_{int} = (n/n-1)^{1/2}\left[F_0^2 - F_0(mean)^2\right] \Big/ \sum F_0^2$$

$$R_1 = \sum ||F_0| - |F_c|| \Big/ \sum |F_0| \qquad WR_2 = \left\{\sum \left[w\left(F_0^2 - F_c^2\right)^2\right] \Big/ \sum \left[w\left(F_0^2\right)^2\right]\right\}^{1/2}$$

$$GooF = \left\{\sum \left[w\left(F_0^2 - F_c^2\right)^2\right] \Big/ (n-p)\right\}^{1/2} \qquad \text{where } n = \text{No. of reflections}, \quad p = \text{No. of refined parameters}$$

2.2. Electron microprobe analyses

The chemical composition was then determined on the same crystal fragment as used for the structural study at the Eugen F. Stumpfl laboratory (Leoben University), using a Superprobe Jeol JXA 8200, operated in the WDS mode, at 20 kV accelerating voltage and 10 nA beam current. The beam diameter was about 1 μm. Synthetic NiAs and Sb_2S_3 were used as standards for Ni, As, S and Sb, whereas Fe was calibrated on natural pyrite. The following X-ray lines were used in the analyses: Kα for Fe, Ni, S and $L\alpha$ for As and Sb. The counting time for peak and both backgrounds (left and right) were 20 and 10 s, respectively. All possible peak overlaps among the selected X-ray emission lines were checked and automatically corrected, using the on-line procedure. The same instrument was used to obtain the backscattered electronic image presented in Fig. 1. The average chemical composition (mean of 7 analyses on different spots), together with the atomic ratios [on the basis of Σ(As + Fe + Sb) = 2 atoms per formula unit (a.p.f.u.), see below], are reported in Table 4.

Table 2
Atoms, site occupancy factors (s.o.f.), fractional atom coordinates (Å), and equivalent isotropic displacement parameters (Å^2) for the selected orcelite crystal.

Atom	s.o.f.	x	y	z	U_{iso}
Ni_1	$Ni_{1.00}$	0	0	0.9475(3)	0.0125(7)
Ni_2	$Ni_{1.00}$	1/3	2/3	0.0998(2)	0.0120(5)
Ni_3	$Ni_{1.00}$	0.2435(3)	0	0.1218(2)	0.0126(3)
Ni_4	$Ni_{1.00}$	0.6304(4)	0	0.2142(1)	0.0122(5)
Ni_5	$Ni_{1.00}$	0.3118(3)	0	0.3213(2)	0.0119(4)
Ni_6	$Ni_{0.75(2)}$	0.6123(4)	0	0.4396(2)	0.0125(6)
As_1	$As_{0.94(3)}Sb_{0.06}$	0	0	0.2501(2)	0.0114(6)
As_2	$As_{1.00}$	1/3	2/3	0.2977(1)	0.0138(4)
As_3	$As_{0.95(3)}Fe_{0.05}$	0.6693(4)	0	0.0234(1)	0.0133(3)