

LETTER

Crystal structure of glaucodot, (Co,Fe)AsS, and its relationships to marcasite and arsenopyrite

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ABSTRACT

The crystal structure of glaucodot, (Co,Fe)AsS, an important member of the FeAsS-CoAsS-NiAsS system, was determined with single-crystal X-ray diffraction. It is orthorhombic with space group $Pn2_1m$ and unit-cell parameters $a = 14.158(1)$, $b = 5.6462(4)$, $c = 3.3196(2)$ Å, and $V = 265.37(5)$ Å³. The structure is closely related to that of arsenopyrite or alloclasite, and represents a new derivative of the marcasite-type structure. The As and S atoms in glaucodot, which are ordered into six distinct sites (As1, As2, As3, S1, S2, and S3), form three types of layers [S, As, and mixed (S + As) layers] that are stacked along a in the sequence of (S + As)-(S + As)-S-(S + As)-(S + As)-As-(S + As)-(S + As)... In contrast, arsenopyrite contains the mixed (S + As) layers only and alloclasite consists of isolated S and As layers only. There are no As-As or S-S bonds in glaucodot; all dianion units are formed between S and As, like those in arsenopyrite and alloclasite. The (Co + Fe) cations in glaucodot occupy three nonequivalent octahedral sites (M1, M2, and M3), with M1(As₅S), M2(As₃S₃), and M3(AsS₅), which form three distinct edge-shared octahedral chains, A, B, and C, parallel to c , respectively. These chains are arranged along a in the sequence of A-A-B-C-C-B-A-A... Whereas the configurations of the A and C chains are analogous to those in safflorite and marcasite, respectively, the configuration of the B chain matches that in alloclasite, leading us to propose that the M1, M2, and M3 sites are predominately occupied by Co, (Co + Fe), and Fe, respectively. Our study, together with previous observations, suggests that glaucodot is likely to have an ideal stoichiometry of (Co_{0.5}Fe_{0.5})AsS, with a limited tolerance for the variation of the Co/Fe ratio.

Keywords: Glaucodot, Co-Fe sulfarsenide, marcasite-type mineral, crystal structure, single-crystal X-ray diffraction

INTRODUCTION

The ternary FeAsS-CoAsS-NiAsS system contains several important sulfarsenides, including arsenopyrite FeAsS, cobaltite CoAsS, gersdorffite NiAsS, alloclasite (Co,Fe)AsS, and glaucodot (Co,Fe)AsS. These minerals are commonly found in complex Co-Ni-As deposits, such as Håkansboda, Sweden (Carlson and Bleeker 1988), the Cobalt District, Ontario (Petruk et al. 1971), Bou-Azzer, Morocco (Ennaciri et al. 1995), Modum, Norway (Grorud 1997), and Spessart, Germany (Wagner and Lorenz 2002). When precipitated from hydrothermal solutions, these sulfarsenides, along with pyrite/marcasite (FeS₂), can incorporate considerable amounts of trace metals, especially so-called “invisible” gold (e.g., Palenik et al. 2004). Under oxidizing conditions, however, they can release significant amounts of arsenic into natural water and soils, in some cases producing serious arsenic poisoning and contamination (O’Day 2006). Therefore, the crystal structures and bonding models of sulfarsenides have been the subject of extensive experimental and theoretical studies (e.g., Vaughan and Rosso 2006; Makovicky 2006)

The crystal structures of all minerals, except glaucodot, in the FeAsS-CoAsS-NiAsS system have been determined. Topologically, each can be categorized into either a modified pyrite- or

marcasite-type structure (Hem et al. 2001; Makovicky 2006). A common structural feature of these minerals is that each cation (M = Fe, Co, and/or Ni) is octahedrally coordinated by six anions (X = As and S), and each anion is tetrahedrally bonded to another anion plus three cations. The diversity of structural symmetries is attributed primarily to the octahedral linkage and the order-disorder of As and S anions.

By analogy to marcasite, de Jong (1926) first derived an orthorhombic cell ($a = 6.67$, $b = 3.21$, and $c = 5.73$ Å) for glaucodot from X-ray powder diffraction data. Using rotating crystal and Weissenberg methods, Ferguson (1947) also obtained an orthorhombic cell for the glaucodot sample from Håkansboda, Sweden, but with $a_0 = 6.64$, $b_0 = 28.39$, and $c_0 = 5.64$ Å, and space group $Cmmm$. Nevertheless, Ferguson (1947) noticed numerous systematically missing reflections that were not due to space-group extinctions and suggested that the whole pattern of reflections can be referred, without abnormal extinctions, to two congruous subcells: Subcell I corresponding to the strong reflections with a P -lattice and $a_1 = a_0/2$, $b_1 = b_0/2$, and $c_1 = c_0$, and subcell II corresponding to the weak reflections with a C -lattice and $a_2 = a_0$, $b_2 = b_0/3$, and $c_2 = c_0$. The subcell II actually matches the pseudo-orthorhombic lattice of arsenopyrite (Buerger 1936; Morimoto and Clark 1961; Fuess et al. 1987). The powder diffraction data given by Ferguson (1947), which

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are in good agreement with those given by Harcourt (1942) for glaucodot from the same locality, however, can all be indexed based on subcell I. Petruk et al. (1971) examined powder X-ray diffraction data on glaucodot from the Cobalt-Gowganda ores and found extra reflections compared to those reported by Ferguson (1947). Sulfarsenides with compositions $(\text{Fe}_{0.75}\text{Co}_{0.25})\text{AsS}$, $(\text{Fe}_{0.96}\text{Co}_{0.04})\text{AsS}$, and $(\text{Co}_{0.82}\text{Fe}_{0.18})\text{AsS}$ from Håkansboda were examined by Cervelle et al. (1973) and by Töpel-Schadt and Mieke (1982) and Kratz et al. (1986). Their results show that Fe-rich sulfarsenides are arsenopyrite, whereas the Co-rich mineral may be cobaltite or alloclasite. Since then, no detailed crystallographic study on glaucodot has been reported. In this paper, we present the first structure solution of glaucodot using single-crystal X-ray diffraction and describe its structural relationships with the marcasite-type sulfarsenide minerals.

EXPERIMENTAL METHODS

The glaucodot specimen used in this study is from Håkansboda and is in the collection of the RRUFF project (deposition No. R070294; <http://truff.info/R070294>), donated by Mike Scott. The chemical composition was determined with a CAMECA SX50 electron microprobe. The average composition (15 point analyses), normalized to $S = 1.0$, yielded a formula of $(\text{Co}_{0.52}\text{Fe}_{0.47}\text{Ni}_{0.01})_{\Sigma=1}\text{As}_{1.00}\text{S}_{1.00}$.

Based on optical examination and X-ray diffraction peak profiles, a nearly equidimensional crystal was selected and mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation. X-ray diffraction data were collected with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of an orthorhombic unit-cell (Table 1). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. Examination of the systematic absences of reflections suggests possible space group $Pnmm$ (no. 59) or its subgroup $Pn2_1m$ (no. 31). A non-standard setting was chosen to facilitate the direct comparison with the structures of marcasite, alloclasite, and arsenopyrite. SHELX97 (Sheldrick 2007) was used for both structure determinations and refinements. No structure solution with R factors $< 20\%$ could be obtained using space group $Pnmm$. The final crystal structure was solved and refined with space group $Pn2_1m$ (Table 1). No significant inversion twin component was detected during the refinements. The refined Flack parameter was 0.06(3). Because of the similarities in X-ray scattering powers for Co, Fe, and Ni, all cations were assumed to be Co and their site occupancies were not determined during the refinements. However, these site occupancies were estimated through other means discussed below. Final coordinates and displacement parameters of all atoms are listed in Table 2, and selected bond distances in Table 3.

RESULTS AND DISCUSSION

The unit-cell parameters of glaucodot in this study are consistent with those for subcell I given by Ferguson (1947). The

TABLE 1. Summary of crystal data and refinement results for glaucodot

Structural formula	$(\text{Co}_{0.52}\text{Fe}_{0.47}\text{Ni}_{0.01})_{\Sigma=1}\text{As}_{1.00}\text{S}_{1.00}$
Crystal size (mm)	$0.06 \times 0.06 \times 0.08$
Space group	$Pn2_1m$ (no. 31)
a (Å)	14.158(1)
b (Å)	5.6462(4)
c (Å)	3.3196(2)
V (Å ³)	265.37(5)
Z	6
ρ_{calc} (g/cm ³)	6.175
λ (Å)	0.71069
μ (mm ⁻¹)	28.31
θ range for data collection	3.89–35.05
No. of reflections collected	4057
No. of independent reflections	1214
No. of reflections with $I > 2\sigma(I)$	1095
No. of parameters refined	62
R_{int}	0.019
Final R factors [$I > 2\sigma(I)$]	$R_1 = 0.020$, $wR_2 = 0.053$
Final R factors (all data)	$R_1 = 0.023$, $wR_2 = 0.054$
Goodness-of-fit	1.093

topology of its crystal structure is similar to that of arsenopyrite or alloclasite and can be regarded as a derivative of the marcasite type. In all of these structures, anions (As and S) display distorted hexagonal closest-packing, stacked along a , and cations (Fe, Co, and Ni) occupy half of the interstitial octahedral sites. The major structural differences among these minerals are shown in Figure 1. The As and S atoms in alloclasite form isolated layers (S layer and As layer) alternating along a , whereas they form mixed layers (S + As layer) in arsenopyrite. The As and S anions in glaucodot, on the other hand, are completely ordered into six crystallographically distinct sites (As1, As2, As3, S1, S2, and S3) and form all three types of layers, which are stacked along a in a sequence of As-(S + As)-(S + As)-S-(S + As)-(S + As)-As... This ordering of anions results in the reduction of the symmetry from $Pnmm$ for marcasite to $Pn2_1m$ for glaucodot and concomitantly triples the length of the a cell edge. Nonetheless, the relative arrangement of S and As atoms in the mixed (S + As) layer in glaucodot is different from that in arsenopyrite, as illustrated in Figure 2. Intriguingly, if we replace the mixed (S + As) layers in arsenopyrite with those in glaucodot and vice versa, we can then obtain two hypothetical structures, one with the arsenopyrite cell and space group $P\bar{1}$, and the other with the glaucodot cell (but double c -dimension) and space group $P2_1$. Furthermore, the relative arrangement of As and S atoms in glaucodot points to the possibility for other stacking sequences of anionic layers in sulfarsenides.

A remarkable feature of the glaucodot structure is that, despite the complicated ordering pattern of S and As atoms, there is no S-S or As-As bonding. All anion-anion bonds, ranging from 2.327(1) to 2.345(1) Å, are between S and As, as also found in arsenopyrite, alloclasite, and ordered cobaltite and gersdorffite. Thus, this observation seems to suggest that S-As bonding is energetically favorable over S-S or As-As bonding in sulfarsenides. Although the average bond angles for all tetrahedrally coordinated anions are essentially alike ($\sim 109.2^\circ$), the individual bond angles within each tetrahedron vary significantly, from ~ 89 to $\sim 123^\circ$. Similar results are also found in other sulfarsenides. Measured in term of tetrahedral quadratic elongation and angle variance (Robinson et al. 1971), the three As tetrahedra in glaucodot are all appreciably more distorted than the three S tetrahedra (Table 3) and the other As and S tetrahedra in alloclasite and arsenopyrite.

There are three symmetrically nonequivalent octahedral cation sites (M1, M2, and M3) in glaucodot, with M1 bonded by 5 As + 1 S, M2 by 3 As + 3 S, and M3 by 1 As + 5 S. The individual M-S and M-As bond distances vary from 2.231(2) to 2.304(1) Å and from 2.306(1) to 2.368(1) Å, respectively, agreeing well with those observed in other (Fe,Co)-bearing

TABLE 2. Coordinates and displacement parameters of atoms in glaucodot

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}
M1	0.0867(1)	0.6831(2)	0	0.0097(2)	0.0041(3)	0.0042(3)	0.0209(4)	-0.0004(2)
M2	0.2524(1)	0.2042(1)	1/2	0.0078(3)	0.0051(4)	0.0018(4)	0.0165(5)	-0.0004(3)
M3	0.4196(1)	0.6836(2)	0	0.0048(2)	0.0035(3)	0.0041(3)	0.0069(3)	-0.0006(2)
As1	-0.0215(1)	0.5574(1)	1/2	0.0065(2)	0.0085(3)	0.0038(3)	0.0073(3)	0.0003(3)
As2	0.1905(1)	0.8228(1)	1/2	0.0064(2)	0.0084(3)	0.0038(3)	0.0071(3)	0.0001(3)
As3	0.3533(1)	0.0636(1)	0	0.0060(2)	0.0064(3)	0.0045(3)	0.0071(3)	-0.0013(3)
S1	0.1495(1)	0.3206(3)	0	0.0070(3)	0.0081(6)	0.0060(6)	0.0070(5)	-0.0011(5)
S2	0.3197(1)	0.5667(3)	1/2	0.0042(2)	0.0058(5)	0.0023(5)	0.0046(5)	0.0000(5)
S3	0.4843(1)	0.3126(3)	0	0.0048(3)	0.0058(6)	0.0037(6)	0.0050(5)	0.0011(5)

Notes: $U_{13} = U_{23} = 0$ for all atoms are zero due to the site symmetry. U_{ij} are in units of Å².

sulfarsenides. With increasing number of bonded As atoms, the mean cation-anion distance for an M octahedron increases, while the degree of octahedral distortion measured by the angle variance decreases (Table 3). There is a good positive correlation between the mean M-anion distance and the U_{eq} parameters for the M cations (Table 2), suggesting that M1 is weakly bonded and M3 strongly bonded.

There exist three distinct edge-shared octahedral chains, A, B, and C, extending parallel to c in glaucodot (Fig. 3), where A, B, and C represent chains made of the M1, M2, and M3 octahedra, respectively. These chains are arranged along a in the sequence of A-A-B-C-C-B-A-A... Interestingly, if the single S atom in the M1 octahedron is switched with the single As atom in the M3 octahedron, then the configurations of the A and C chains are analogous to those in safflorite $CoAs_2$ and marcasite FeS_2 , respectively. The configuration of the B chain corresponds well to that in alloclasite $(Co,Fe)AsS$. Accordingly, the structure of glaucodot may be considered as a mixture of FeS_2 (marcasite) + $(Co,Fe)AsS$ (alloclasite) + $CoAs_2$ (clinosafflorite or safflorite).

The existence of the three kinds of octahedral chains in glaucodot raises an open question regarding the possible ordering of Fe and Co among the three M sites. Theoretical calculations based on molecular orbital and band models (Vaughan and Rosso 2006) have shown that the marcasite-type chains made of MS_6 octahedra will become destabilized when Co enters the octahedral site, as its addition will introduce electrons into the anti-bonding e_g^* band. This explains why CoS_2 (cattierite) crystallizes in the pyrite-type, rather than marcasite-type, structure in nature. Because the C-chain corresponds to the marcasite type, we postulate a dominant preference of Fe in the M3 site in glaucodot. For an edge-shared MA_6 octahedron, molecular orbital theory predicts that, due to the interaction between the $3d\sigma(e_g)$ orbitals of M^{2+} and the π_p orbitals of As_2^{2-} , the Fe-As-Fe angle subtending the M-M separation across the shared octahedral

TABLE 3. Selected interatomic distances (Å) in glaucodot

	Distance	Distance	Distance
M1-S1	2.231(2)	As1-M1 ×2	2.368(1)
M1-As1	2.307(1)	As1-M1	2.306(1)
M1-As1 ×2	2.368(1)	As1-S1	2.345(1)
M1-As2 ×2	2.353(1)	S1-M1	2.231(2)
Average	2.330	S1-M2 ×2	2.304(1)
PAV	4.4	S1-As1	2.345(1)
PQE	1.002	Average	2.347
		PAV	152.6
		PQE	1.037
		Average	2.296
		PAV	115.5
		PQE	1.027
M2-S1 ×2	2.304(1)	As2-M1 ×2	2.353(1)
M2-S2	2.258(2)	As2-M2	2.325(1)
M2-As2	2.325(1)	As2-S2	2.332(2)
M2-As3 ×2	2.330(1)	S2-M2	2.258(2)
Average	2.308	S2-M3 ×2	2.279(1)
PAV	7.1	S2-As2	2.332(2)
PQE	1.002	Average	2.340
		PAV	158.0
		PQE	1.038
		Average	2.287
		PAV	118.8
		PQE	1.028
M3-S2 ×2	2.279(1)	As3-M2 ×2	2.330(1)
M3-S3 ×2	2.267(1)	As3-M3	2.342(1)
M3-S3	2.286(2)	As3-S3	2.327(1)
M3-As3	2.342(1)	S3-M3	2.286(2)
Average	2.286	S3-M3 ×2	2.266(1)
PAV	9.2	S3-As3	2.327(1)
PQE	1.003	Average	2.332
		PAV	163.3
		PQE	1.030
		Average	2.287
		PAV	123.6
		PQE	1.030

Note: PAV = polyhedral angle variance in degrees squared; PQE = polyhedral quadratic elongation (Robinson et al. 1971).

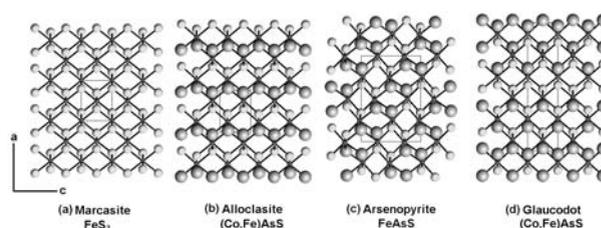


FIGURE 1. Comparison of crystal structures of (a) marcasite, (b) alloclasite, (c) arsenopyrite, and (d) glaucodot. Large, medium, and small spheres represent As, S, and M (=Fe + Co + Ni) atoms, respectively.

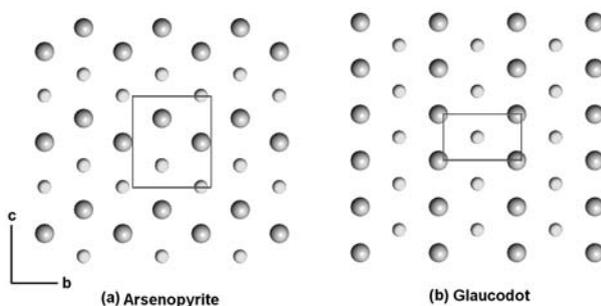


FIGURE 2. Comparison of the mixed (As + S) anionic layers in (a) arsenopyrite and (b) glaucodot.

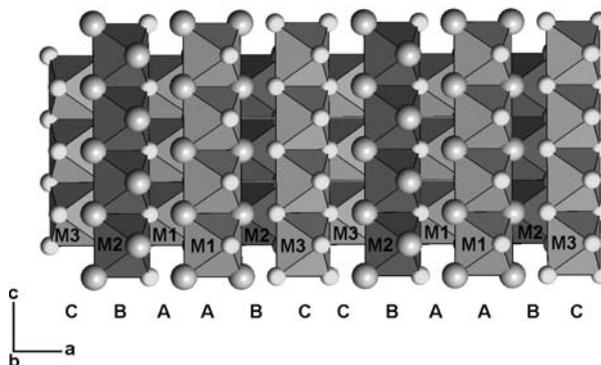


FIGURE 3. Polyhedral view of the glaucodot structure. Large and small spheres represent As and S atoms, respectively. The A, B, and C chains, made of the edge-shared M1, M2, and M3 octahedra, respectively, are arranged along a in the sequence of A-A-B-C-C-B-A-A...

edge should be substantially smaller than the Co-As-Co angle, resulting in the so-called “compressed marcasite-type” structure (Tossell et al. 1981; Tossell 1984). Indeed, this angle is 74° in $FeAs_2$ löllingite (Lutz et al. 1987), but 83° in $CoAs_2$ safflorite (Yang et al. 2008). In $CoAs_2$ clinosafflorite, the Co-As1-Co and Co-As2-Co angles are 73.5 and 92.3° , respectively (Kjekshus 1971), with an average value of 83° . The two different Co-As-Co angles in clinosafflorite is ascribed to the effective bond types of $Co^{3+}-As1$ and $Co^{2+}-As2$ (Tossell et al. 1981). The respective M1-As1-M1 and M1-As2-M1 angles subtending the M1-M1 separation in glaucodot are 89.0 and 89.7° . These two angles are markedly greater than the Fe-As-Fe angle in löllingite, or the Co-As-Co angle in safflorite, and close to the Co-As2-Co angle in clinosafflorite, thus pointing to the strong Co^{2+} enrichment in

the M1 site in glaucodot, consistent with the arguments that the valence of Fe, Co, and Ni cations in pyrite- and marcasite-type disulfides, diarsenides, and sulfarsenides is 2+, rather than 3+ or 4+ (Vaughan and Rosso 2006 and references therein). For the M2 octahedron in glaucodot, the respective M2-S1-M2 and M2-As3-M2 angles subtending the M2-M2 separation are 92.2 and 90.9°, both of which are smaller than the corresponding angles ($\angle M-S-M = 93.6^\circ$ and $\angle M-As-M = 95.3^\circ$) in alloclasite with $M = 0.76 \text{ Co} + 0.21 \text{ Fe} + 0.03 \text{ Ni}$ (Scott and Nowacki 1976), suggesting that the M2 site in glaucodot should contain more than 21% Fe. Accordingly, we propose an ideal crystal-chemical formula for glaucodot as $\text{Co}^{M1}(\text{Co,Fe})^{M2}\text{Fe}^{M3}(\text{AsS})_3$.

The formation conditions and stability relations of glaucodot with respect to arsenopyrite and cobaltite have been a matter of discussion. Because glaucodot could not be synthesized in the FeAsS-CoAsS-NiAsS system at 650 °C for 8 days or 600 °C for 17 days, Klemm (1965) concluded that this mineral might be a metastable phase. Yet, further investigation by Bayliss (1969) shows that glaucodot was only partially converted to cobaltite even after 30 days at 630 ± 20 °C, suggesting sluggish kinetics for the transformation between glaucodot and cobaltite and providing an explanation for the experimental results of Klemm (1965). From the crystal-chemical point of view, the more complex ordering arrangement of As and S atoms in glaucodot compared to arsenopyrite or alloclasite could imply a prolonged thermal process for the formation of this mineral. Currently, based on the relative contents of Fe vs. Co, there are no defined chemical boundaries to distinguish arsenopyrite, glaucodot, alloclasite, and cobaltite along the FeAsS-CoAsS join. For example, Töpel-Schadt and Mieke (1982) referred to $(\text{Fe}_{0.96}\text{Co}_{0.04})\text{AsS}$ and $(\text{Co}_{0.82}\text{Fe}_{0.18})\text{AsS}$ as glaucodot, despite that neither of them exhibited the glaucodot unit-cell parameters and that $(\text{Fe}_{0.75}\text{Co}_{0.25})\text{AsS}$ and $(\text{Co}_{0.76}\text{Fe}_{0.21}\text{Ni}_{0.03})\text{AsS}$ have been demonstrated to be arsenopyrite (Cervelle et al. 1973) and alloclasite (Scott and Nowacki 1976), respectively. Törmänen and Koski (2005) assumed sulfarsenides between $(\text{Fe}_{0.25}\text{Co}_{0.75})\text{AsS}$ and $(\text{Fe}_{0.75}\text{Co}_{0.25})\text{AsS}$ to be glaucodot, while the ideal chemical formula for this mineral in the International Mineralogical Association nomenclature documentation (January 2008) is CoAsS. A survey of the literature shows that glaucodot appears to always contain nearly equal amounts of Fe and Co atoms (e.g., Ferguson 1947; Gammon 1966; Petruk et al. 1971). The glaucodot sample in this study is another example of this stoichiometry. This observation, together with the fact that glaucodot is often found as exsolved lamellae inter-grown with arsenopyrite and/or alloclasite (e.g., Gammon 1966; Petruk et al. 1971), indicates that glaucodot is most likely to have an ideal chemistry of $(\text{Co}_{0.5}\text{Fe}_{0.5})\text{AsS}$ with a restricted variation in the Co/Fe contents in glaucodot.

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