

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