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STRUCTURAL AND PHYSICAL PROPERTIES OF FISCHESSERITE, A RARE GOLD–SILVER SELENIDE FROM THE DE LAMAR MINE, OWYHEE COUNTY, IDAHO, USA

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ABSTRACT

Fischesserite, Ag_3AuSe_2, from the De Lamar mine, Owyhee County, Idaho, USA, was chemically and structurally analyzed. Electron-microprobe analyses give the chemical formula $Ag_{2.98}Cu_{0.01}Au_{0.97}Se_{2.03}$. Fischesserite is optically isotropic, silver white in color with a metallic luster. In reflected light, the mineral is pink. Where observed near naumannite, it appears darker with slightly bluish tints. Reflectivity values are 32.5 (471.1 nm), 30.0 (548.3 nm), 31.1 (586.6 nm), and 33.7% (652.3 nm). Fischesserite is cubic, space group $I4_132$, with a 9.965(1) Å, V 989.5(2) Å^3 and $Z = 8$. The crystal structure has been refined to R = 2.69%. Fischesserite exhibits a garnet-like structure consisting of edge-sharing $Ag[Se_4Ag_2Au_2]$ and $Au[Ag_6Se_2]$ polyhedra. Fischesserite is confirmed to be isotypic with petzite, Ag_3AuTe_2. The different crystal-chemical environments of noble metals in fischesserite and petzite are compared with those found in other silver–gold chalcogenides.

Keywords: fischesserite, Ag–Au chalcogenides, chemical composition, physical properties, crystal- structure refinement, De Lamar mine, Owyhee County, Idaho.

SOMMAIRE

Nous avons caractérisé la composition et la structure de la fischesserite, Ag_3AuSe_2, provenant de la mine De Lamar, comté d'Owyhee, en Idaho. Les analyses effectuées avec une microsonde électronique ont donné comme formule chimique $Ag_{2.98}Cu_{0.01}Au_{0.97}Se_{2.03}$. La fischesserite est optiquement isotrope, de couleur blanc argent avec un éclat métallique. En lumière réfléchie, le minéral est rose, mais près de la naumannite, il semble plus foncé avec une teinte légèrement bleuâtre. Les valeurs de réflectivité sont 32.5 (471.1 nm), 30.0 (548.3 nm), 31.1 (586.6 nm), et 33.7% (652.3 nm). La fischesserite est cubique, groupe spatial $I4_132$, avec a 9.965(1) Å, V 989.5(2) Å^3 et $Z = 8$. Sa structure cristalline a été affinée jusqu'à un résidu R de 2.69%. Elle est faite de polyèdres à arêtes partagées de $Ag[Se_4Ag_2Au_2]$ et $Au[Ag_6Se_2]$ agencés dans un motif ressemblant à un grenat. La fischesserite est confirmée être isotypique de la petzite, Ag_3AuTe_2. Les différents milieux cristallochimiques des atomes de métaux nobles dans la fischesserite et la petzite sont comparés avec ceux qui caractérisent les chalcogénures de l'or et de l'argent.

(Traduit par la Rédaction)

Mots-clés: fischesserite, chalcogénures de Au et Ag, composition chimique, propriétés physiques, affinement de la structure, mine De Lamar, comté d'Owyhee, Idaho.

INTRODUCTION

Fischesserite, Ag_3AuSe_2, was established as a mineral species by Johan *et al.* (1971) during a study of ore minerals in the carbonate veins of the uranium-bearing selenium deposit of Předbořice, Bohemia, Czech Republic. Johan *et al.* supplied a detailed chemical and physical characterization of the mineral, and described it as the first naturally occurring selenide of gold. On the basis of its strong chemical and structural similarities to the mineral petzite, Ag_3AuTe_2, Johan *et al.* (1971) concluded that fischesserite is the selenium analogue of petzite. Although unit-cell parameters were obtained from X-ray powder-diffraction data, a structure determination was not done at that time. Since then, two sulfoselenides of gold have been reported: petrovskaite, AgAu(S,Se) (Nesterenko *et al.* 1984), and penzhinite, $Ag_4Au(S,Se)_4$ (Bochek *et al.* 1984), but their structures still have not been determined. In order to study the crystal-chemical behavior of selenium in the presence

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of gold and to test whether fischesserite is isostructural with petzite, we present new crystal-structure data for fischesserite from the De Lamar mine, Owyhee County, Idaho, USA, together with physical, optical, and chemical data.

OCCURRENCE

The sample (catalogue number 45109/G) containing the mineral fischesserite used in this study was obtained from the mineralogical collection of the Natural History Museum of the University of Florence. The associated minerals are naumannite, covellite and pyrite, whereas the gangue mineral is calcite. The mineral occurs as anhedral to subhedral grains up to 300 μm across. It does not show any inclusions of other minerals or intergrowths.

PHYSICAL AND OPTICAL PROPERTIES

Fischesserite, a silver white mineral, has a metallic luster. The micro-indentation measurements carried out with a VHN load of 25 g gave a mean value of 31 kg/mm^2 (range: 28–34), corresponding to a Mohs hardness of about 2–2½. This finding is in excellent agreement with that found by Johan *et al.* (1971) for fischesserite from the type locality at Předbořice, Czech Republic (31.9 kg/mm^2).

In reflected light, fischesserite is pink in color and isotropic. Where observed near naumannite, it is darker and shows a pink color with slightly bluish tints. No evidence of growth zonation is observed.

Reflectance measurements were performed in air using a MPM–200 Zeiss microphotometer equipped with a MSP–20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Measurements of reflectivity (in %) are 32.5 (471.1 nm), 30.0 (548.3 nm), 31.1 (586.6 nm), and 33.7 (652.3 nm).

In Figure 1, we show the good agreement between the reflectance percentages obtained for the De Lamar fischesserite with those measured by Johan *et al.* (1971) for type-locality fischesserite.

CRYSTAL-STRUCTURE REFINEMENT

A crystal fragment measuring 80 × 90 × 120 μm was selected for a single-crystal X-ray-diffraction study. The unit-cell parameter, determined by centering 25 high-θ (22–25°) reflections on an automated diffractometer (Bruker P4), is: *a* 9.965(1) Å, *V* 989.5(2) Å^3. In-

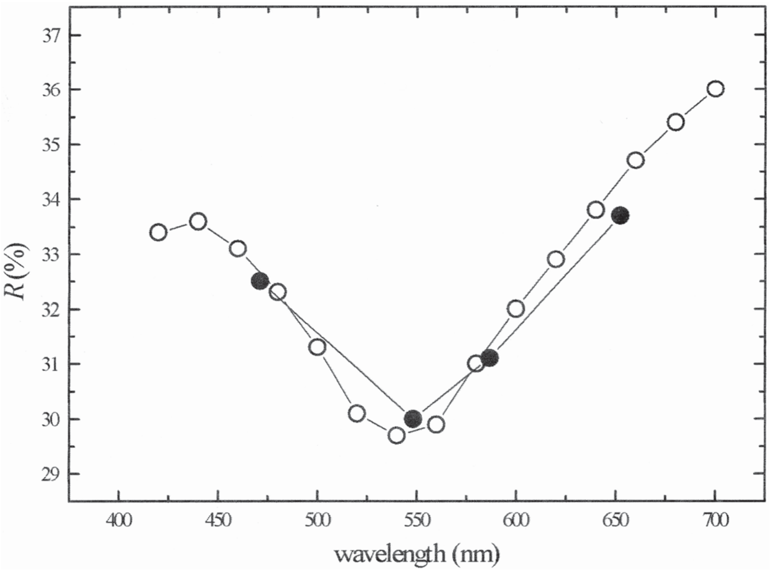

FIG. 1. Reflectivity curves for fischesserite samples in air. Open symbols refer to fischesserite from Předbořice (Johan *et al.* 1971), filled symbols refer to fischesserite from the De Lamar mine.

TABLE 1. FRACTIONAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN FISCHESSERITE

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Ag	0.3626(1)	0	¼	0.0232(4)	0.0232(5)	0.0233(4)	0	0	0.0003(3)	0.0232(3)
Au	⅛	⅛	⅛	0.0242(3)	U_{11}	U_{11}	0.0003(2)	U_{12}	U_{12}	0.0242(3)
Se	0.2756(1)	0.2756(1)	0.2756(1)	0.0255(4)	U_{11}	U_{11}	-0.0001(3)	U_{12}	U_{12}	0.0255(4)

TABLE 2. X-RAY POWDER-DIFFRACTION PATTERNS FOR FISCHESSERITE

	1		2	
hkl	d_{calc} (Å)	I/I_{calc}	d_{obs} (Å)	I/I_0
110	7.046	39	7.08	6
220	3.5232	1	3.501	1
310	3.1512	4	3.153	3
222	2.8766	16	2.877	4
321	2.6633	100	2.662	10
411	2.3488	8	2.349	5
330	2.3488	14		
420	2.2282	29	2.229	8
422	2.0341	22	2.035	8
510	1.9543	14	1.954	6
431	1.9543	17		
521	1.8194	22	1.820	8
440	1.7616	6	1.763	2
530	1.7090	1	1.708	1
622	1.5023	7	1.501	4
631	1.4693	9	1.469	5
444	1.4383	8	1.439	4
543	1.4093	5	1.410	3
710	1.4093	2		
640	1.3819	5	1.382	3
721	1.3561	3	-	-
642	1.3316	6	1.332	6
651	1.2656	10	1.266	7
732	1.2656	10		
800	1.2456	6	1.246	3
741	1.2266	1	1.227	2
554	1.2266	4		
743	1.1584	3	1.159	2
750	1.1584	1		
662	1.1431	2	-	-
752	1.1283	6	1.130	3
833	1.1005	1	-	-
842	1.0873	3	-	-
761	1.0746	1	-	-
921	1.0746	1	-	-
851	1.0504	2	-	-
763	1.0278	2	-	-
932	1.0278	4	-	-
941	1.0066	1	-	-
853	1.0066	1	-	-

1: *d* values calculated on the basis of $a = 9.965(1)$ Å and with the atomic coordinates reported in Table 2. Intensities calculated using XPOW software, version 2.0 (Downs *et al.* 1993). 2: observed powder-diffraction pattern and indexing originally reported by Johan *et al.* (1971).

tensity data were collected using Mo$K\alpha$ radiation monochromatized with a flat graphite crystal in ω-scan mode. Intensities were corrected for Lorentz–polarization effects and for absorption following the semi-empirical method of North *et al.* (1968); the values of the equivalent pairs were averaged. The merging *R* for the ω-scan dataset decreased from 22.12% before the absorption correction to 3.32% after this correction. The structure refinement was performed in the space group $I4_132$, starting from the atom coordinates for natural Ag_3AuTe_2 (Frueh 1959), using the program SHELXL–97 (Sheldrick 1997). The introduction of anisotropic temperature-factors for all the atoms led to $R = 2.69\%$ for 324 observed reflections [$F_o > 4\sigma(F_o)$] and $R = 4.38\%$ for all 412 independent reflections. Neutral scattering curves for Ag, Au and Se were taken from *The International Tables of X-ray Crystallography*, volume IV (Ibers & Hamilton 1974). The difference-Fourier map revealed maximum positive and negative peaks of 1.99 and 2.24 $e^-/Å^3$, respectively. Fractional coordinates of the atoms and anisotropic-displacement parameters are shown in Table 1. A list of the observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

In Table 2, the X-ray powder pattern originally observed for the type material (Johan *et al.* 1971) is compared with that calculated using the structural parameters obtained in this study. Calculated and observed data match closely.

CHEMICAL COMPOSITION

The crystal fragment of fischesserite used for the structural study was analyzed with a JEOL JXA–8600 electron microprobe. Concentrations of the major and minor elements were determined at 20 kV accelerating voltage and 40 nA beam current, with variable counting times: 30 s were used for Au, Ag and Se, and 60 s for the minor elements Fe, Cu, S and Te. For the wavelength-dispersion analyses, the following lines were used: Au$M\alpha$, Ag$L\alpha$, Se$L\alpha$, Fe$K\alpha$, Cu$K\alpha$, S$K\alpha$, and Te$L\alpha$. The estimated analytical precision (in wt.%) is: ±0.15 for Au, ±0.20 for Ag and Se, ±0.02 for Fe and Cu, ±0.03 for S and Te. The standards employed were pure elements for Au, Ag, Se, Cu, marcasite for Fe, galena for S, and synthetic Sb_2Te_3 for Te. The crystal fragment was found to be homogeneous within the analytical error. The average chemical composition (15 analyses on different spots), together with ranges of wt.% of elements, is reported in Table 3. On the basis of 6 atoms, the empirical formula of fischesserite is $Ag_{2.98}Cu_{0.01}Au_{0.97}Se_{2.03}$, and ideally Ag_3AuSe_2.

RESULTS AND DISCUSSION

Fischesserite is a member of the petzite group (Strunz & Nickel 2001). There are three members in this group: uytenbogaardtite, Ag_3AuS_2 (Barton *et al.* 1978), fischesserite, Ag_3AuSe_2 (Johan *et al.* 1971), and petzite, Ag_3AuTe_2 (Frueh 1959). The crystal structure of petzite was determined by Frueh (1959) and subsequently reexamined by Chamid *et al.* (1978). It has a garnet-like structure consisting of edge-sharing $Ag[Se_4Ag_2Au_2]$ and $Au[Ag_6Se_2]$ polyhedra. The crystal structure of fischesserite is topologically identical to that of petzite, apart from the slight deviations expected from the size of the anions (*i.e.*, Se with respect to Te). The silver atoms are tetrahedrally surrounded by Se atoms, with two of the Se atoms at 2.775(1) Å and two at 2.891(1) Å. The coordination sphere is completed by two Au atoms [2.951(1) Å] and two Ag atoms [2.954 Å] (Fig. 2a). The gold atoms have two close selenium atoms [2.599(2) Å] and six Ag atoms at 2.951(1) Å (Fig. 2b). Interestingly, the Au–Se distance is longer than the Au–Te distance (2.53 Å) in petzite (Frueh 1959). Lastly, each selenium atom is surrounded by six silver atoms [three at 2.775(1) Å and three at 2.891(1) Å] and one gold atom [at 2.599(2) Å].

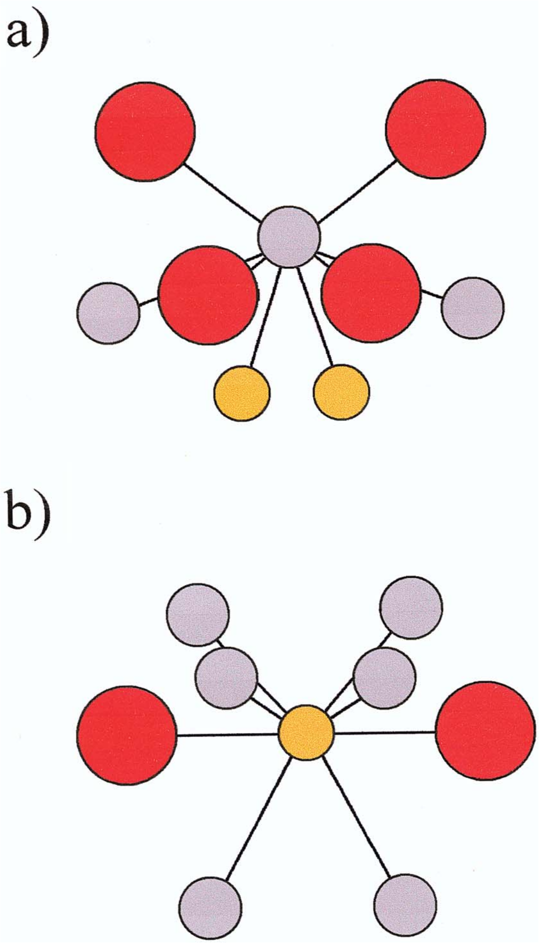

FIG. 2. Silver (a) and gold (b) polyhedra. Gray, dark yellow and red circles refer to Ag, Au and Se atoms, respectively.

In spite of the relative abundance of S, Se and Te in the Earth's crust, the mineral petzite was discovered more than a century earlier than uytenbogaardtite and fischesserite. This can be explained by the pronounced metallic character of Te with respect to Se and S, and consequently, by its greater geochemical affinity with noble metals. In addition, uytenbogaardtite (Ag_3AuS_2), is the only member of the petzite group not having cubic symmetry. The slight distortion of the structure toward a tetragonal symmetry (Barton *et al.* 1978) clearly indicates the difficult adjustment of the sulfur atoms in a nearly intermetallic structure.

It should be noted that the crystal chemistry of noble metals in fischesserite and petzite is quite different from that in the other gold–silver tellurides and selenides: $AgTe_4$ tetrahedra in the crystal structures of hessite (Ag_2Te, Van der Lee & de Boer 1993), stützite ($Ag_{5-x}Te_3$, Peters *et al.* 1996), empressite (AgTe, Bindi *et al.* 2004); $AgTe_6$ and $AuTe_6$ octahedra in the crystal structures of sylvanite ($AgAuTe_4$, Pertlik 1984a), muthmannite ($AuAgTe_2$, Bindi & Cipriani 2004); $AuTe_6$ octahedra in the crystal structures of calaverite ($AuTe_2$, Schutte & de Boer 1988), krennerite ($AuTe_2$, Pertlik 1984b); $AgSe_4$ tetrahedra and $AgSe_3$ triangles in the crystal structure of naumannite (Ag_2Se, Wiegers 1971). The complicated stereochemistry of silver and gold in chalcogenides has been examined by Wiegers (1971) in his study of the crystal chemistry of silver in synthetic compounds having the formula Ag_2X, with X = O, S, Se, and Te. In his pioneering study, Orgel (1958) ascribed the complicated stereochemistry to a mixing

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF FISCHESSERITE FROM THE DE LAMAR MINE, IDAHO

element	wt.%	range	σ (%)
Ag	47.61	47.11 – 47.95	0.20
Cu	0.10	0.00 – 0.18	0.02
Fe	0.02	0.00 – 0.08	0.02
Au	28.31	27.84 – 28.57	0.15
Se	23.75	23.02 – 24.15	0.20
Te	0.02	0.00 – 0.09	0.03
S	0.02	0.00 – 0.05	0.03
total	99.83		

of electrons in the *d* and *s* shells. However, several problems still exist, and additional structural work on the other available gold–silver chalcogenides is needed to shed light on the system Ag–Au–Te–Se.

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