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THE CRYSTAL STRUCTURE AND CALCULATED POWDER-DIFFRACTION DATA FOR ZVYAGINTSEVITE, Pd_3Pb

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ABSTRACT

The crystal structure of zvyagintsevite, Pd_3Pb, has been re-examined using a single-crystal fragment from the Konder ultramafic massif, Far-Eastern Russia. The whole sphere of Mo$K\alpha$ data was collected to $2\theta = 100°$, and the averaged and absorption-corrected unique segment of data was refined to $R = 2.3\%$. An awaruite-type structure is confirmed, space group $Pm\bar{3}m$, with an a of 4.035(1) Å. On the basis of the single-crystal refinement, a fully indexed powder pattern has been calculated.

Keywords: zvyagintsevite, crystal structure, chemical composition, X-ray powder-diffraction data, Konder ultramafic complex, Russia.

SOMMAIRE

Nous avons réexaminé la structure cristalline de la zvyagintsevite, Pd_3Pb, en utilisant un fragment monocristallin provenant du massif ultramafique de Konder, dans la partie d'Extrême Orient de la Russie. Une sphère complète de données de diffraction a été mesurée avec rayonnement Mo$K\alpha$ jusqu'à $2\theta = 100°$. Après calcul de la moyenne des intensités équivalentes et correction d'absorption, l'élément asymétrique a été affiné jusqu'à $R = 2.3\%$. Nous confirmons une structure de type awaruite, avec un groupe d'espace $Pm\bar{3}m$, et un paramètre a égal à 4.035(1) Å. Un diagramme de poudre, complètement indexé, a été calculé à partir des données nouvelles.

Mots-clés: zvyagintsevite, structure cristalline, composition chimique, données de diffraction X, spectre de poudre, roches ultramafiques, massif de Konder, Russie.

INTRODUCTION

Zvyagintsevite, ideally Pd_3Pb, was first described as occurring in massive sulfide ore from the Noril'sk Cu–Ni–PGE (platinum-group elements) deposits, Russia (Genkin *et al.* 1966, Cabri & Traill 1966). The Noril'sk zvyagintsevite is cubic, $Pm\bar{3}m$, with a cell edge a equal to 4.025 Å; synthetic Pd_3Pb has a equal to 4.02$_4$ Å (Cabri & Traill 1966). The composition of zvyagintsevite was reported to be $Pd_{2.88}Au_{0.12}Pb_{1.0}$ (Cabri & Traill 1966). Genkin *et al.* (1966) reported a composition of $(Pd_{2.50}Pt_{0.18}Fe_{0.09}Ni_{0.08}Cu_{0.08})_{\Sigma 2.93}(Pb_{0.58}Sn_{0.49})_{\Sigma 1.07}$ for the Noril'sk mineral, and Genkin *et al.* (1969) found that zvyagintsevite from the nearby Talnakh deposit has a composition $Pd_{2.98}Pb_{1.02}$. It was also found in the PGE-bearing ores of the Stillwater Complex, Montana; Laflamme (1976) reported its composition to be $(Pd_{2.97}Pt_{0.03}Ni_{0.01})_{\Sigma 3.01}(Pb_{0.97}Hg_{0.02})_{\Sigma 0.99}$.

Recently, unusually large crystals of zvyagintsevite (up to 8 mm on a side) have been reported from the Konder alkaline-ultramafic massif in the Ayan-Maya region of the northern part of Khabarovsk Territory, about 200 km west of the Sea of Okhotsk, Russia (Gebhard *et al.* 1996, Cabri & Laflamme 1997). The unit-cell edge of the Konder zvyagintsevite is 4.036 Å (Cabri & Laflamme 1997), larger than that of synthetic Pd_3Pb owing to the Pt content. The geology and mineralogy of the Konder massif and the related placers, which are reported to contain large crystals of zvyagintsevite and ferroan platinum, are described by Nekrasov *et al.* (1994) and Sushkin (1995). Because the only data in the Powder Diffraction File (PDF) pertain to synthetic Pd_3Pb of Cabri & Traill (1966), it was considered that quantitative analyses of a fragment of one of the large crystals of zvyagintsevite, together with a crystal-structure determination, would be useful. Pearson's

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Handbook (Villars & Calvert 1991) lists the data from Ellner (1981) and gives the cell edge a of the synthetic material [4.035(1) Å], the space group ($Pm\bar{3}m$, No. 221), and the atomic coordinates. However, without a knowledge of the individual isotropic thermal parameters, a true powder-diffraction pattern cannot be calculated.

Experimental

A fragment of a large crystal of zvyagintsevite (crystal "A" of Cabri & Laflamme 1997) was cut with a scalpel to produce an orthogonal crystal, 0.18 × 0.18 × 0.12 mm. Smaller off-cuts from the same fragment were used to obtain a confirmation of the powder pattern (ICDD No. 20–827) of the synthetic material by means of a RIGAKU microdiffractometer. The fragment was mounted on an Enraf-Nonius CAD-4 single-crystal diffractometer. The cell dimension was obtained from a refinement of the diffraction angles of 38 reflections in the range $60° < 2\theta < 80°$, measured using Mo$K\alpha$ graphite-monochromated X-radiation. Diffraction data were collected at a speed of 1°/min (2θ) using the DIFRAC software (White & Gabe 1992), with profile analysis to a limit of $2\theta = 100°$. The whole sphere was collected in segments corresponding to the 48 equivalents of ($h \geq k \geq l$). Empirical absorption-corrections were applied using the ψ-sweep method (North *et al.* 1968) in conjunction with an average correction for the mean thickness of the crystal. Data reduction resulted in 100 unique reflections, all of which were "observed" on the criterion that $I_{obs} \geq 2.5 \times \sigma(I_{obs})$. The crystal data are given in Table 1. After data collection, the crystal was chemically analyzed by wavelength-dispersion spectrometry using a JEOL 733 electron microprobe, operated at 20 kV with a beam current of 20 nA (cup reading) using a finely focused beam. The following X-ray emission lines and standards were used: Pd$L\alpha$ and Pb$L\alpha$ (synthetic Pd_3Pb), Pt$L\alpha$ and Fe$K\alpha$ (synthetic PtFe), Ir$L\alpha$, Os$L\alpha$, Ni$K\alpha$, Cu$K\alpha$ and Bi$M\alpha$ (Ir, Os, Ni, Cu and Bi pure metals). Counting time was of the order of 20–60 s, and data correction was done using a conventional ZAF routine.

Eight spot-analyses were done on the crystal. The average and standard deviation of these findings are given in Table 2. The intervals for the averages were calculated using a 90% confidence limit.

TABLE 1. CRYSTAL DATA FOR ZVYAGINTSEVITE

a 4.035(1) Å	V 65.695(3) Å^3
Crystal size (mm): 0.18 × 0.18 × 0.12	μ(Mo$K\alpha$) = 899.2 cm^{-1}
Space group: $Pm\bar{3}m$ (221)	Z = 1
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\| = 2.31\%$	
Structure:	
$(Pd_{0.96}Pt_{0.04})$ at ½,½,0; U = 0.01473(17) Å^2 [B = 0.997(13) Å^2]	
$(Pb_{0.89}Bi_{0.11})$ at 0,0,0; U = 0.01262(13) Å^2 [B = 1.163(10) Å^2]	
Composition: $(Pd_{2.88}Pt_{0.12}Cu_{<0.01})_{\Sigma 3.01}(Pb_{0.88}Bi_{0.11})_{\Sigma 0.99}$	
X-ray data: whole sphere of reflection collected to $2\theta = 100°$ with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.70932 Å). 4800 reflections collected; 100 unique reflections, none "unobserved".	

Structure Determination

In accordance with the microprobe results, composite scattering curves were prepared for $(Pd_{0.96}Pt_{0.04})$ and $(Pb_{0.89}Bi_{0.11})$, using the coefficients of Cromer & Mann (1967), with the use of the anomalous scattering components of Cromer & Liberman (1970). The structure was refined to an agreement factor of $R = 2.3\%$. With both atomic sites at special positions, there are only three parameters to be determined in the structure analysis: the two isotropic displacement-parameters and a scale factor. An attempt to include an extinction coefficient in the least-squares refinement was unsuccessful; the coefficient refined to a small negative value. Attempts to refine the atomic proportions within each site also were unsuccessful. The final displacement-parameters (U in Å^2) are given in Table 1. The software used in structural analysis was the NRCVAX package for PC computers (Gabe *et al.* 1989).

Description of the Structure

The $AuCu_3$ structure type (gold group, awaruite subgroup) described in Villars & Calvert (1991) is confirmed. In space group $Pm\bar{3}m$, the (Pb,Bi) atom occurs at the origin (0,0,0), and the (Pd,Pt) atom occurs at (½,½,0). This results in twelve-fold coordination of the Pb atom by the Pd atoms, and of square-planar coordination of the Pd atom by the Pb atoms. The Pd–Pb distance is 2.853(1) Å. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Cell Edge of Zvyagintsevite

Nowotny *et al.* (1946) reported that synthetic Pd_3Pb has a cubic Cu_3Au structure, and crystallizes in space group $Pm\bar{3}m$, with a equal to 4.013_5 Å. Cabri & Traill

TABLE 2. CHEMICAL COMPOSITION OF ZVYAGINTSEVITE FROM THE KONDER MASSIF, RUSSIA

	Pd	Pt	Cu	Pb	Bi	Total
Ave. (wt.%)	57.62	4.29	0.03	34.08	4.15	100.17
Std dev.	0.36	0.05	0.01	0.27	0.11	
+/–	0.25	0.04	0.005	0.19	0.08	

* Ir, Os, Fe and Ni were sought, but were not detected. The minimum detection-limits were 0.09, 0.07, 0.02 and 0.02 wt.%, respectively.

(1966) reported a cell edge a of 4.02_4 Å from Debye–Scherrer film work on synthetic Pd_3Pb. Ellner (1981) reported 4.035 Å for his synthetic material. The mineral used here contains 4% atomic substitution of Pt for Pd and 11% atomic substitution of Bi for Pb. The interatomic distances in the metallic phases of the four elements are: 2.749 Å for Pd–Pd (King & Manchester 1978), 2.775 Å for Pt–Pt (Waseda *et al.* 1975), 3.501 Å for Pb–Pb (Klug 1946), and 3.072 Å for Bi–Bi (Schiferl & Barrett 1969). It is evident that the substitution of Pt for Pd will increase the cell edge, whereas the substitution of Bi for Pb will decrease it. The value obtained here for zvyagintsevite is fortuitously the same as that given by Ellner (1981). Recently, Cabri & Laflamme (1997) reported a cell edge a of 4.036 Å from a 114.6-mm Gandolfi camera pattern of a fragment from the same crystal as used in the present study. It seems that the earlier values of 4.013_5 and 4.02_4 Å must be inaccurate (an apparent 2θ-shift caused by the extreme absorption [μ(Cu$K\alpha$) = 2929 cm^{-1}] would account for this), and a value of 4.035(1) Å should be accepted both for this mineral and for the synthetic product.

Calculated Powder-Pattern for Zvyagintsevite

After the structure refinement was completed, the parameters listed in Table 1 were used to calculate the powder pattern for zvyagintsevite for Cu$K\alpha$ radiation up to 2θ = 140°, using the software routine DISPOW in the NRCVAX system of programs (Gabe *et al.* 1989). The data are listed in Table 3.

TABLE 3. CALCULATED POWDER-DIFFRACTION DATA FOR ZVYAGINTSEVITE

Zvyagintsevite, naturally occurring mineral from the Konder massif, Russia.
Ideally, monolead tripalladium, $PbPd_3$
Composition: $(Pd_{2.89}Pt_{0.12}Cu_{<0.01})_{\Sigma 3.01}(Pb_{0.88}Bi_{0.11})_{\Sigma 0.99}$

Rad: Cu$K\alpha$	Lambda: 1.54060 Å	I/Icor: 18.8
System: cubic	Space group: $Pm\bar{3}m$ (221)	
a: 4.035(1) Å	Z = 1	
Dx: 13.58 g•cm^{-3}	Dm: 13.32 g•cm^{-3} (Cabri & Traill 1966)	

Powder pattern calculated for Cu$K\alpha$ radiation from parameters obtained in single-crystal structure determination from full sphere of Mo$K\alpha$ data.
$AuCl_3$ type, Gold group, awaruite subgroup.
PSC: cP4. Mwt: 526.4. Volume[CD]: 65.69

d Å	Int. I	Peak I	$h\,k\,l$	2θ
4.035	7	8	1 0 0	22.011
2.8532	6	6	1 1 0	31.326
2.3296	100	100	1 1 1	38.617
2.0175	47	45	2 0 0	44.892
1.8045	3	3	2 1 0	50.539
1.6473	3	2	2 1 1	55.760
1.4266	26	23	2 2 0	65.362
1.3450	1	1	2 2 1, 3 0 0	69.879
1.2760	1	1	3 1 0	74.270
1.2166	28	23	3 1 1	78.567
1.1648	8	7	2 2 2	82.800
1.1191	1	1	3 2 0	86.994
1.0784	1	1	3 2 1	91.172
1.0087	4	3	4 0 0	99.568
0.9786	1	1	3 2 2, 4 1 0	103.834
0.9511	1	1	4 1 1, 3 3 0	108.180
0.9257	14	10	3 3 1	112.637
0.9023	14	10	4 2 0	117.244
0.8805	1	1	4 2 1	122.051
0.8603	1	<1	3 3 2	127.125
0.8236	17	8	4 2 2	138.533

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