American Mineralogist, Volume 65, pages 154–156, 1980

Crystal structure refinement of a cobaltian ullmannite

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Abstract

A crystal structure refinement of a cobaltian ullmannite (Ni,Co)SbS, which has a pyrite-type structure with ordering of Sb and S, has been refined to a *R* value of 0.023 in space group $P2_13$. No conclusive evidence for deviations from cubic symmetry was found.

Introduction

The crystal structure of ullmannite (NiSbS) was initially proposed by Ramsdell (1925); in this structure Sb is substituted in one set of four sites occupied by S in the NiS_2 pyrite-type crystal structure. This reduces the cubic symmetry from *Pa*3 to the non-centric $P2_13$, which allows the atoms to move along the three-fold axes. This crystal structure was confirmed by Peacock and Henry (1948) and Bokij and Tsenokev (1954), and later refined by Takéuchi (1957). Recently Bayliss (1977a) refined an arsenian ullmannite, Ni(Sb,As)S, which is optically anisotropic and where an ordered substitution of Sb by As reduced the symmetry to *P*1. Therefore we decided to check if the substitution of Ni by Co would cause a loss of symmetry in ullmannite like that reported by Bayliss and Stephenson (1968) for a cobaltian gersdorffite. A cobaltian ullmannite (D27860) from Broken Hill, New South Wales, was obtained from the Australian Museum for this study.

Experimental and results

The sample was analyzed by electron microprobe as previously described by Stout and Bayliss (1975). The analytical results and derived chemical formula based upon a 4AXY model are presented in Table 1. This composition is close to the end-member composition of ullmannite, except for the substitution of Ni by Co. The sample was optically isotropic.

A 114.6 mm Debye-Scherrer photograph was taken with nickel-filtered Cu radiation. A unit cell with $a = 5.9218$A was calculated by the Nelson and Riley (1945) extrapolation method to $\theta = 90°$. All reflections can be indexed in space group $P2_13$. In addition this unit-cell value lies within the experimental values of Bayliss (1969) for $Ni_{0.9}Co_{0.1}SbS$ of 5.926A and $Ni_{0.8}Co_{0.2}SbS$ of 5.911A.

A single crystal $120 \times 70 \times 60$ μm was selected because of its well-developed cube form {100}. This crystal was aligned on a precession camera using Mo radiation along an a^* axis. Photographs *hk*0 and *h*0*l* showed no systematic absences or deviation from a cubic unit cell.

The crystal was accurately centered on a four-circle diffractometer with reflections 800, $\bar{8}00$ and 080 so that a^* axis coincided with the diffractometer ϕ axis. Integrated intensities of all reflections from one hemisphere were collected with Mo$K\alpha$ radiation and a graphite 002 monochromator. Within the range $5° < 2\theta < 60°$, 1235 reflections were scanned in duplicate with the $\omega : 2\theta$ scan mode at $1°$ 2θ per minute over the scan width of $1.7° + \tan\theta$. Normally, 10-second background counts were measured at both the beginning and end of each reflection, except where the total counts were less than 500; background counts were then measured for 60 seconds to obtain better data. A standard reflection 020 was measured every 50 reflections throughout the data collection in order to check experimental stability.

Background, Lorentz, polarization, and absorption corrections were made by the method of Wuensch and Prewitt (1965). The linear absorption coefficient of this cobaltian ullmannite is 231.3 cm^{-1}, which results in transmission factors between 0.21 and 0.33 for this crystal. The extinction factor described by Zachariasen (1967) and extended by Coppens and Hamilton (1970) was calculated.

From one hemisphere, 131 symmetry-independent reflections with 129 reflections above the 1σ level

Table 1. Electron microprobe analysis and atomic proportions

Atom	Weight % NiSbS	Weight % D27860	Atomic Proportions	
Ni	27.6	23.3	0.86	1.00
Co		3.8	0.14	
Sb	57.3	58.9	1.00	1.00
			0.02	1.00
As		0.4	0.01	
S	15.1	14.8	0.97	
	100.0	101.2		

were measured in space group $P2_13$, which has systematic absences of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd. All reflections were included in the refinement of the crystal structure by the least-squares program (RFINE4) of Finger and Prince (1975). All observations were weighted according to $w = 1/\sigma_F^2$, where σ_F is the standard deviation based on counting statistics. Initial positional parameters were taken from Takéuchi (1957). The neutral atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (1974). The data were first refined in space group $P2_13$ to an R value of 0.023. The positional parameters, isotropic temperature factors, and extinction parameter are listed in Table 2. These values are similar to those of arsenian ullmannite reported in Table 2 of Bayliss (1977a). The final R values of the isotropic and anistropic model are the same.

This R value indicates that the crystal structure is basically correct, but space group $P2_13$ has systematic absences of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd; however, these reflections were observed (Table 3). The only space group which allows all reflections to be observed with this crystal structure is $P1$ similar to gersdorffite (Bayliss and Stephenson, 1968), arsenian ullmannite (Bayliss, 1977a), and anisotropic pyrite (Bayliss, 1977b). The data were then refined in space group $P1$, but showed no difference from previous refinements. Table 4 gives the interatomic distances and angles for the cubic ($P2_13$) refinement. These values are similar to those of arsenian ullmannite reported in Table 4 of Bayliss (1977a).

Table 2. Positional parameters, isotropic temperature factors, and extinction parameter

Atom	Site Occupancy	x	B(A^2)
Ni	Ni 0.86 Co 0.14	-0.0178(1)	0.56(2)
S	S 0.97 As 0.01 Sb 0.02	0.3816(2)	0.83(3)
Sb	Sb 1.00	0.6264(1)	0.55(1)

Extinction parameter -0.000018(1)

Table 3. Observed structure factors

$h\ k\ l$	F_o	$h\ k\ l$	F_o	$h\ k\ l$	F_o
1 0 0	5.0(1)	3 0 0	3.3(5)	5 0 0	12(2)
0 1 0	4.2(1)	0 3 0	4.1(3)	0 5 0	12(2)
0 0 1	1.7(1)	0 0 3	9.7(5)	0 0 5	2(4)

Discussion

All the atoms in the cubic crystal structure ($P2_13$) of ullmannite occupy special positions on one of the three-fold axes in a group of four; therefore any small movement of any atom from a three-fold axis or an ordering process within any group of four atoms will cause most of the symmetry to disappear. Therefore the refinement indicates that the cobalt atoms have randomly substituted for the nickel atoms in this crystal structure.

Although the weak odd-order reflections ($h00$, $0k0$, and $00l$) are present, they may be caused by the misuse or malfunction of the electronics (Szymański, 1979). However, since only 35kV was used, the electronics effect as described should not be observed. These weak odd-order reflections were measured at a position to avoid the Renninger effect. The crystal structure refinement of the $P1$ model is similar to the $P2_13$ model and the mineral is optically isotropic. Therefore if these weak odd-order reflections do indicate a movement of atoms from their position on the three-fold axis, then this movement is below the detection limit of this crystal structure refinement and the optical measurement.

The substitution of Co for Ni in this cobaltian ullmannite, (Ni,Co)SbS, does not distort the crystal structure as does the substitution of Co for Ni in the cobaltian gersdorffite (Ni,Co)AsS, described by Bay-

Table 4. Interatomic distances and angles

Atom	Distance (A)	Atom	Angle (°)
Ni - S	2.376	S - Ni - S	99.5
Ni - Sb	2.553	S - Ni - Sb	83.4
S - Sb	2.511	Sb - Ni - Sb	90.5
		Ni - S - Ni	116.7
		Ni - Sb - Ni	116.6
		Ni - S - Sb	100.5
		Ni - Sb - S	100.7

liss and Stephenson (1968). The probable explanation is that the greater size difference of Sb and S compared to As and S causes more ordering within ullmannite than gersdorffite, since gersdorffite has been observed in both the ordered (Bayliss and Stephenson, 1967) and disordered (Bayliss, 1968) forms, whereas ullmannite has only been observed in the ordered form.

Acknowledgments

Financial assistance was provided by the National Research Council of Canada. Mr. B. Rutherford did the electron probe analysis. Dr. C. T. Prewitt critically reviewed the manuscript.

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Manuscript received, May 11, 1979;
accepted for publication, September 13, 1979.