Discovery of Stolzite in China and Refinement of Its Crystal Structure

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Abstract

Although stolzite was discovered in Yaogangxian, Hunan Province, China, in 1948, no formal report about this mineral has been published. Recently its crystal structure has been refined by means of the Rietveld method. The cell dimensions of the mineral are: $a=b=0.544503(3)$ nm, $c=1.20495(1)$ nm and $\alpha=\beta=\gamma=90°$. The X, Y and Z coordinates of the atom O refined by the authors are 0.2637, 0.1137 and 0.0706, respectively. The length of the W-O bond is 0.17826 nm and the angle of the O-W-O bound are 123° and 103°, respectively.

Key words: stolzite, Rietveld method, refinement of crystal structure, Yaogangxian, Hunan Province

1 Course of Discovery

Stolzite is a secondary mineral occurring in the oxidizing zone of the tungsten deposit. No formal report of the mineral has been published yet in China. When Xu Keqin and Ji Shouyuan made an investigation in a wolframite mine at Yaogangxian, Zixing, Hunan, in the summer of 1947, they discovered the first skarn-type scheelite deposit of China at Heshangtan on the southeast side of this mine (Xu, 1957). In the summer of the next year, Xu Keqin together with Jin Wanlin again went to Heshangtan, Yaogangxian, to carry out geological and topographic surveys in the scheelite district and stayed in Lin's residence. They found some small yellow crystals in sludges and clays beside a shallow gully on a hill slope about 200-300 m east of this residence. The blowpipe analysis in the field indicated that this kind of crystal contained lead and tungstate radicals. According to its chemical composition combined with its crystal form, colour and other physical properties, this kind of crystal was named stolzite.

Xu and Jin excavated and collected clays and sludges with small yellow crystals and recovered about 200 g of the crystals through washing. The crystals still maintained a very perfect form though they were washed. According to their mode of occurrence in the field, it may be considered that this kind of stolzite is a secondary mineral formed by tungsten in scheelite in skarns and lead in sulphides such as galena under oxiding conditions.

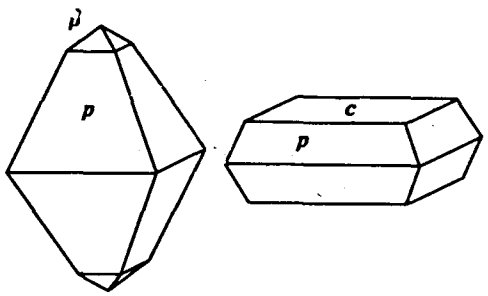

Fig. 1 Crystal form of Yaogangxian stolzite
p-{101}; c-{001}; β-{103}.

2 Mineralogical Features

Stolzite from Yaogangxian has a well-developed crystal form and is present in combinations of tetragonal dipyramids {101} and {103} or flat combinations of tetragonal dipyramids {101} (Fig. 1). Colour, orange-yellow; luster, vitreous to adamantine; cell dimension, <2 mm. The chemical composition is given by the electron microprobe energy dispersion analysis in Table 1.

In the middle 1960s, Xue Jiyue studied stolzite of Yaogangxian using the X-ray Debye method and proved that the specimen collected by Xu et al. in 1948 was really stolzite. Table 2 shows the D-spacings of Yaogangxian stolzite. The cell dimensions obtained using X-ray powder are $a=b=$ 0.544503(3) nm and $c=$ 1.20495(1) nm. Under the stereoscopic microscope stolzite may be observed to contain dust-like impurities. The impurities are also visible on the single-crystal precession X-ray photographs or Weissenberg photographs, and there even appear multi-crystal rings of the impurity phase in the selected-area electron diffraction pattern. From the data of the X-ray powder diffraction, it may be concluded that the impurity phase is not the single phase, and among other things grossular is the most important mineral phase. The multi-crystal diffractions of the impurity phase on the single-crystal X-ray diffraction pattern are clear and sharp lines, so it is estimated that its grain size is of the order of μm and that the mineral was enclosed when stolzite crystallized.

3 Experiments Method for Refining the Crystal Structure

Although the crystal form of Yaogangxian stolzite is well developed, its diffraction peaks are too wide to use the X-ray four-circle diffractometer to refine the crystal structure. We tried to use this method to analyse 15 crystals, but to no avail; we failed. So we could not but use the Rietveld method (Rietveld, 1969) for refining the crystal structure.

The diffraction data were gathered on a D/MAX-ⅢB instrument made in Japan, with CuKα radiation, voltage 40 KV, tube current 25 mA, and step width of the step scaning 0.04° . A total of 343 intensity data were gathered within the range of this angle. The refinement of the structure was carried out using the IDBWS-9006 PC procedure of R.A. Young.

As stated above, stolzite contains the inseparable impurity phase. The diffraction peaks of both do not overlap with each other and the intensity of the strongest peak of the impurity phase is lower than 2% in comparison with that of stolzite. Therefore the data of diffraction intensity of the original diagram were not treated at the beginning of refinement. The experimental values of strong peaks of stolzite fit the theoretical values very well when

Table 1 Electron Microprobe Energy Dispersion Analysis of Stolzite from Yaogangxian

Analytical item	WO_3	PbO	MgO	FeO *	CoO	NiO	
1	49.98	49.53	0.21			0.12	99.84
2	50.26	48.44	0.27			0.12	99.09
3	47.93	50.54	0.16	0.16	0.10		98.89
4	48.45	51.87	0.24	0.11			100.6
Mean	49.16	50.10	0.22	0.08	0.02	0.06	
Total standard deviation	0.98	1.27	0.04	0.06	0.05	0.08	

* Total iron.

Table 2 D-Spacings of Yaogangzian Stolzite

d	*I*	*hkl*	*d*	*I*	*hkl*
'3.358	1	-	1.257	7	332
3.325	100	112	1.243	8	404
#3.114	1	-	1.22	5	420
3.015	32	004	1.188	3	228
* 2.959	1.5	-	1.15	3	1.1.10
2.731	44	200	1.131	5	424
* 2.646	5	-	1.083	3	336
2.487	<1	202	1.054	5	512
* 2.417	<1	-	1.011	3	408
2.392	2	211	1.004	<1	0.0.12
2.378	<1	114	0.988	3	3.1.10
* 2.298	<1	-	0.984	2	523
2.207	1	105	0.948	2	428
2.088	1	213	0.944	5	516
2.023	40	204	0.942	3	1.0.12
1.93	15	220	0.925	3	552
* 1.905	<1	-	#0.916	1	-
1.782	31	116	0.909	<1	600
1.717	1	215	0.891	2	2.2.12
1.659	30	312	0.879	2	3.3.10
1.625	15	224	0.87	2	604
#1.592	1	-	0.866	2	2.1.13
* 1.58	<1	-	0.862	1	620
1.507	3	008	0.848	3	536
1.364	3	400	0.846	<1	509
1.319	9	208	0.841	2	1.1.14
1.309	22	316	0.84	<1	615
1.305	<1	109	0.829	2	624
1.287	<1	325	0.827	<1	3.0.10
* 1.282	<1	-			

Note: those with * are produced by grossular; those with' are possibly produced by quartz; "#" denotes other impurity phases.

the R value is reduced to 0.07. Therefore the diffraction of the impurity phase exerts little influence on the refinement of the crystal structure of stolzite.

Table 3 Parameters of Stolzite Crystal Structure

Item	Ion	Ion coordinates of $PbWO_4$ of Yaogangxian refined in the paper			Ion coordinates of $PbWO_4$ reported by Wyckoff		
		O	W	Pb	O	W	Pb
Coordinates	X	0.2637	0	0	0.25	0	0
	Y	0.1137	0	0	0.13	0	0
	Z	0.0706	0	0.5	0.075	0	0.5
Temperature factor	B11	0.119963	0.009672	0.000138	Absent in literature		
	B22	0.021598	0.000000	0.000000			
	B33	0.013782	0.001523	0.000801			
	B12	0.090943	0.000000	0.000000			
	B13	0.016086	0.000000	0.000000			
	B23	0.005081	0.000000	0.000000			

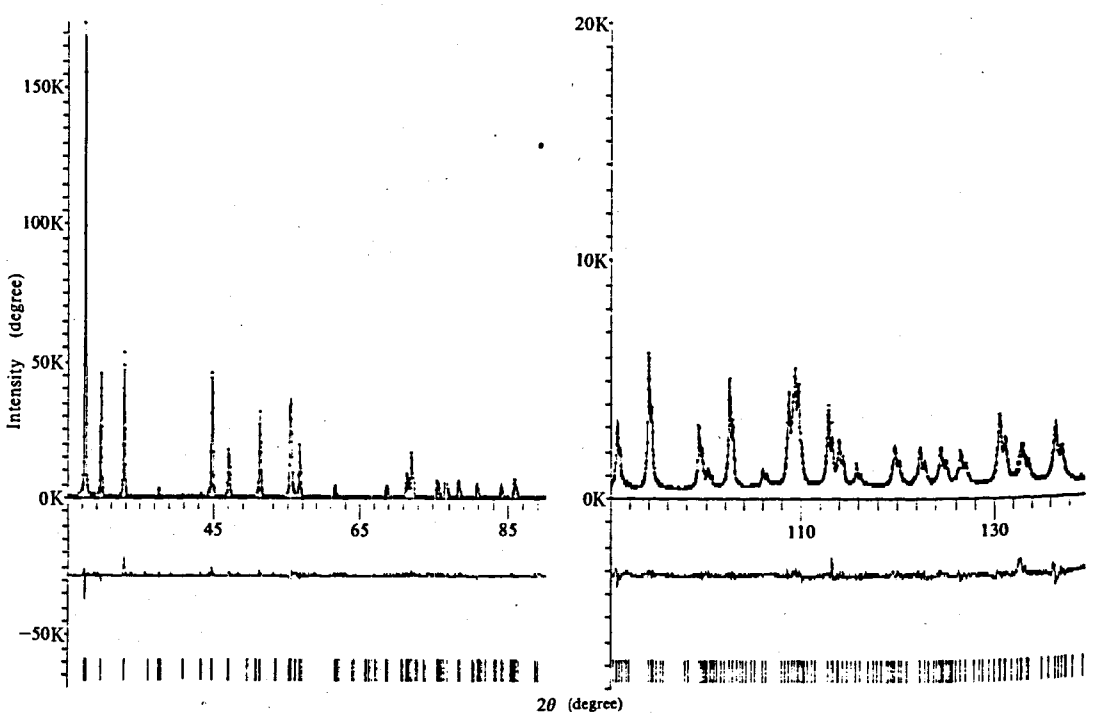

Fig. 2 Diffraction intensity distribution of stolzite by computer fitting

The upper line-observed diffraction intensity; the lower line-calculated diffraction intensity; middle-difference diagram between observed intensity and calculated intensity; lower-positions of diffractions

4 Results and Discussion

Since Wyckoff (1951) reported that stolzite crystals belong to the scheelite structure in 1931, the authors have not found that the crystal structure of stolzite was refined. Table 3 shows the comparison between the parameters of the crystal structure determined by the authors and the parameters of Wyckoff. The W and Pb atoms are in the 4a and 4b positions of 4 and the O atoms are in general positions of 16.

The deviation factor RI value of the stolzite crystal structure determined by the authors is 4.48% and the RF value is 3.85%. Fig. 2 shows the observed diffraction intensity obtained by computer fitting and the diffraction intensity obtained by calculating the parameters of the crystal structure as well as the difference diagram of both. Fig. 3 shows the stereo model of the crystal structure of stolzite.

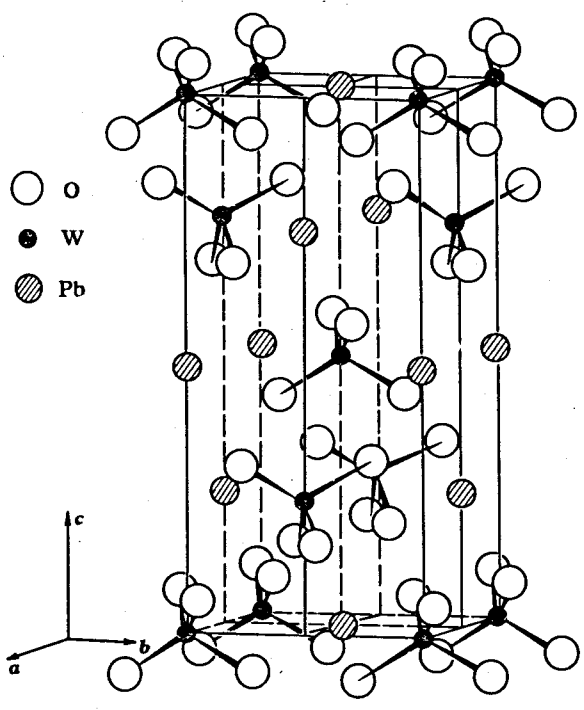

Fig. 3 Crystal structure model of stolzite

In summary, the authors have the following understandings of the crystal structure of stolzite: ① stolzite is tetragonal, space group $I4_1/a$, with $a=b=$ 0.544503(3) nm and $c=$ 1.20495(1) nm, and has the same structure as scheelite; ② the X, Y and Z coordinates of the atom O, which were originally 0.25, 0.13 and 0.075 respectively, have been refined by the authors and are now 0.2637, 0.1137 and 0.0706 respectively; ③ the W-O tetrahedron in the new structure shows D_{2d} symmetry, with a W-O separation of 0.17826 nm and O-W-O angles of 123° and 103°.

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