

## ZEMANNITE, A ZINC TELLURITE FROM MOCTEZUMA, SONORA, MEXICO

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### ABSTRACT

Zemannite occurs as minute hexagonal prisms terminated by a bipyramid. The mineral is light to dark brown, has an adamantine lustre, and is brittle. It is uniaxial positive:  $\omega=1.85$ ,  $\epsilon=1.93$ . The density is greater than  $4.05 \text{ g/cm}^3$ , probably about  $4.36 \text{ g/cm}^3$ . Crystal structure study gave the following: space group  $P6_3/m$ ,  $a$   $9.41 \pm 0.02$ ,  $c$   $7.64 \pm 0.02 \text{ \AA}$ ,  $Z=2$ . Zemannite is a zeolite-like tellurite with a negatively charged framework of  $[\text{Zn}_2(\text{TeO}_3)_3]$  having large (diam. =  $8.28 \text{ \AA}$ ) open channels parallel to  $[0001]$ . These channels are statistically occupied by Na and H ions and possibly by  $\text{H}_2\text{O}$ . Some Fe substitutes for Zn. Partial analyses and the crystal structure analysis indicate the formula  $(\text{Zn,Fe})_2(\text{TeO}_3)_3\text{Na}_x\text{H}_{2-x}\cdot y\text{H}_2\text{O}$ . Strongest lines in the X-ray powder pattern (in  $\text{Å}$ , for  $\text{CuK}\alpha$ ) are:  $8.15(10)$  ( $10\bar{1}0$ ),  $4.07(8)$  ( $20\bar{2}0$ ),  $2.96(6)$  ( $11\bar{2}2$ ),  $2.845(6)$  ( $21\bar{3}1$ ),  $2.778(9)$  ( $20\bar{2}2$ ),  $1.726(6)$  ( $20\bar{2}4$ ,  $22\bar{4}3$ ). The name is in honor of Professor Dr. Josef Zemann, University of Vienna, who has contributed so greatly to our knowledge of the structure of tellurium compounds.

### SOMMAIRE

La zémannite se trouve sous forme de petits prismes hexagonaux bipyramidés. Le minéral varie du brun pâle au brun foncé; son lustre est adamantin. Il est uniaxe positif ( $\omega=1.85$ ,  $\epsilon=1.93$ ) et relativement fragile. Sa densité, supérieure à  $4.05 \text{ g/cm}^3$ , se rapproche probablement de  $4.36 \text{ g/cm}^3$ . Une étude de sa structure cristalline révèle le groupe spatial  $P6_3/m$ , avec  $a$   $9.41 \pm 0.02$ ,  $c$   $7.64 \pm 0.02 \text{ \AA}$ ,  $Z=2$ . La zémannite est un tellurite "zéolitique" qui consiste d'une trame  $[\text{Zn}_2(\text{TeO}_3)_3]$  à charges négatives et de canaux d'un diamètre de  $8.28 \text{ \AA}$  parallèles à  $[0001]$ . Ces canaux contiennent des ions Na et H et même peut-être de l'eau. Le fer substitue pour le zinc. Des analyses partielles ainsi que l'analyse de la structure donnent la formule suivante:  $(\text{Zn,Fe})_2(\text{TeO}_3)_3\text{Na}_x\text{H}_{2-x}\cdot y\text{H}_2\text{O}$ . Les raies les plus intenses dans un cliché de poudre (en  $\text{Å}$ , radiation  $\text{CuK}\alpha$ ) sont:  $8.15(10)$  ( $10\bar{1}0$ ),  $4.07(8)$  ( $20\bar{2}0$ ),  $2.96(6)$  ( $11\bar{2}2$ ),  $2.845(6)$  ( $21\bar{3}1$ ),  $2.778(9)$  ( $20\bar{2}2$ ),  $1.726(6)$  ( $20\bar{2}4$ ,  $22\bar{4}3$ ). Le nom fait honneur à M. le Pro-

fesseur Josef Zemann, de l'Université de Vienne, qui a contribué tellement à nos connaissances des structures des composés de tellure.

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### INTRODUCTION

Zemannite was first recognized as a possible new species by Mandarino & Williams (1961) who referred to it as a zinc tellurite or tellurate. Problems involving the determination of the chemical formula delayed submission of the description to the Commission on New Minerals Names, I.M.A. After the structural determination by Matzat (1967), the description of zemannite was submitted and both the mineral and name were approved. An abstract of the description of zemannite was published by Mandarino *et al.* (1969). The mineral is named in honor of Professor Dr. Josef Zemann, esteemed Austrian crystallographer who has contributed so greatly to our knowledge of tellurium and selenium oxysalts. Type material (milligrams) is preserved in the mineral collections of the Royal Ontario Museum. The type specimen is ROM Number M25933.

### OCCURRENCE AND PHYSICAL PROPERTIES

Zemannite occurs at the Moctezuma mine, near Moctezuma, Sonora, Mexico. Although the individual crystals are very small, zemannite is widespread at the locality. The occurrence is described by Gaines (1965) who has also summarized the mineralogy of the locality (Gaines 1970).

Zemannite occurs as small crystals, usually less than one mm long, which consist of a prism and a bipyramid. The crystals are translucent to transparent, light to dark brown, and have an adamantine lustre and a white streak. Zemannite does not fluoresce under short- or long-wave ultraviolet light. No cleavage was observed. The

hardness was not determined, but the mineral is quite soft and is very brittle. Although the density could not be measured, it was calculated to be about  $4.36 \pm 0.08 \text{ g/cm}^3$ . The method of calculation is given in a later section.

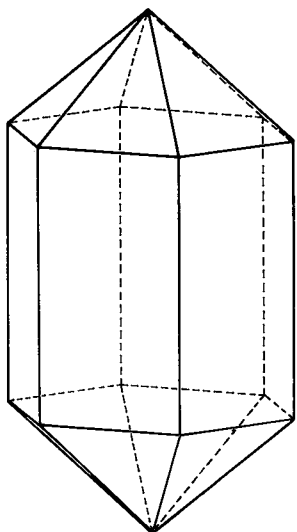


FIG. 1. A typical crystal of zemannite showing the forms  $\{10\bar{1}0\}$  and  $\{10\bar{1}1\}$ .

TABLE 1. X-RAY POWDER DATA FOR ZEMANNITE

$hkl$	$d_{\text{calc}}$	$d_{\text{meas}}$	$I_{\text{est}}$	$hkl$	$d_{\text{calc}}$	$d_{\text{meas}}$	$I_{\text{est}}$
10 $\bar{1}0$	8.150	8.15	10	3143	1.690	1.686	4
10 $\bar{1}1$	5.574			3252	1.679		
11 $\bar{2}0$	4.705	4.69	1/2	5050	1.630		
20 $\bar{2}0$	4.075	4.07	8	2134	1.623	1.622	1
11 $\bar{2}1$	4.006			4152	1.612	1.609	1
00 $\bar{2}0$	3.820	3.80	3	5051	1.594		
20 $\bar{2}1$	3.594			4043	1.591	1.590	2
10 $\bar{1}2$	3.458	3.44	1	3360	1.568		
21 $\bar{3}0$	3.080	3.07	4	3034	1.562	1.563	1/2
11 $\bar{2}2$	2.966	2.96	6	4260	1.540		
21 $\bar{3}1$	2.857	2.845	6	3361	1.536	1.535	1/2
20 $\bar{2}2$	2.788	2.778	9	4261	1.510		
30 $\bar{3}0$	2.717			3253	1.507		
30 $\bar{3}1$	2.560	2.547	3	1015	1.502	1.504	5
10 $\bar{1}3$	2.431			5052	1.499		
21 $\bar{3}2$	2.398	2.390	3	2244	1.483	1.481	2
2240	2.352	2.345	5	5160	1.464		
3140	2.260			3144	1.459		
2241	2.248			4153	1.458	1.455	3
1123	2.240	2.242	1/2	1125	1.453		
3032	2.214	2.207	4	3362	1.451		
3141	2.168			5161	1.438		
2023	2.160	2.160	5	2025	1.431	1.433	2
4040	2.038			4262	1.428	1.424	2
2242	2.003	1.998	3	4044	1.393	1.388	1
4041	1.969			5053	1.373		
2133	1.963	1.952	1/2	2135	1.369		
3142	1.946	1.942	1/2	5162	1.367	1.366	2
0004	1.910	1.906	2	6060	1.358		
3250	1.870			4370	1.340		
1014	1.860	1.855	3	6061	1.337		
3033	1.858			3254	1.336		
3251	1.816	1.812	2	3363	1.336		
4042	1.798	1.792	4	3035	1.332	1.332	1
4150	1.778			4371	1.320		
1124	1.770	1.767	1/2	4263	1.318	1.316	1
4151	1.732			5270	1.305		
2024	1.730						
2243	1.728	1.726	6				

$\text{CuK}\alpha$  radiation, camera diam. 114.6mm, measurements corrected for film shrinkage, ROM specimen number M25933, film No. 3477.

Zemannite is uniaxial positive with  $\omega=1.85$  and  $\epsilon=1.93$ . The mineral is dichroic with  $\omega$  reddish brown and  $\epsilon$  yellowish brown; absorption,  $\omega > \epsilon$ .

#### CRYSTALLOGRAPHY

Zemannite is hexagonal, space group  $P6_3/m - C^2_{6h}$ ,  $a$   $9.41 \pm 0.02$ ,  $c$   $7.64 \pm 0.02 \text{ \AA}$ ,  $c:a = 0.8119$ ,  $V=585.9 \text{ \AA}^3$ ,  $Z=2$ . The crystals are morphologically simple and consist of only two forms:  $\{10\bar{1}0\}$  and  $\{10\bar{1}1\}$ . The habit is usually prismatic, but a few crystals with a very small prism development have been seen. No twinning was observed. The angular relations of the two forms are:  $\{10\bar{1}0\}$ ,  $\phi = 30^\circ 00'$ ,  $\rho = 90^\circ 00'$ ;  $\{10\bar{1}1\}$   $\phi = 30^\circ 00'$ ,  $\rho = 43^\circ 09'$ . A typical crystal is shown in Figure 1.

Full details of the structure of zemannite are given by Matzat (1967). The X-ray powder diffraction data are given in Table 1.

#### CHEMICAL COMPOSITION

A complete chemical analysis was not performed. Partial XRF and electron microprobe analyses indicated that the atomic ratio of Zn to Fe is between 3:1 and 3:2. The atomic ratio of  $(\text{Zn}+\text{Fe})$  to Te is about 2:3. Small amounts of Mn, Mg, and Na were detected, but do not exceed one percent each.

The structural determination by Matzat (1967) showed that zemannite is a zeolite-like tellurite with a negatively charged framework of  $\text{Zn}_2(\text{TeO}_3)_3$  with a large (8.28 $\text{ \AA}$  diameter) channel running parallel to  $[0001]$ . These channels are statistically occupied by Na and H ions and possibly by  $\text{H}_2\text{O}$ . Partial analyses and the crystal structure analysis suggest the formula  $(\text{Zn},\text{Fe})_2(\text{TeO}_3)_3\text{Na}_x\text{H}_{2-x}\cdot y\text{H}_2\text{O}$ , where  $x$  can vary from 0 to 2. Type material is ferroan zemannite.

#### CALCULATION OF DENSITY

Because of the small size of the crystals, it was not possible to measure the density of the mineral. A crystal placed in a liquid with a density of  $4.05 \text{ g/cm}^3$  sank, thus establishing the fact that the density was greater than  $4.05 \text{ g/cm}^3$ . The density of zemannite was calculated in the following manner.

From the unit cell dimensions and the formula  $(\text{Zn},\text{Fe})_2(\text{TeO}_3)_3\text{Na}_x\text{H}_{2-x}\cdot y\text{H}_2\text{O}$ , it is obvious that a range in density can be calculated for each value of  $y$  varying the value of  $x$  between 0 and 2. The lower limit of this range is  $3.705 \text{ g/cm}^3$  where  $x=0$  and  $y=0$ ; i.e. the formula is  $(\text{Zn},\text{Fe})_2(\text{TeO}_3)_3\text{H}_2$  (the amounts of Zn and

TABLE 2. SAMPLE CALCULATION OF THE DENSITY OF  $(Zn_{1.35}Fe_{0.65})(TeO_3)_3NaH \cdot 5H_2O$ 

Constituent	Wt.% = $p$	$k$	$pk/100$	Density from Gladstone-Dale relationship
ZnO	14.35	0.158	0.0227	$\rho = \frac{\bar{n} - 1}{K} = \frac{0.877}{0.200} = 4.38 \text{ g/cm}^3$
FeO	6.10	0.188	0.0115	
TeO <sub>2</sub>	62.55	0.183	0.1145	Density from unit cell
Na <sub>2</sub> O	4.05	0.190	0.0077	$\rho = \frac{MZ}{VA} = \frac{1530.90}{352.89} = 4.34 \text{ g/cm}^3$
H <sub>2</sub> O	12.95	0.340	0.0440	
Total	100.00		0.2004	$M$ = molecular weight
	$M=765.45$		$K=0.200$	$Z$ = number of formula units per unit cell
				$V$ = volume of unit cell
				$A$ = Avogadro's number ( $0.6023 \times 10^{24}$ )

Fe in the formula are, respectively 1.35 and 0.65 throughout this discussion. This is equivalent to an atomic ratio for Zn:Fe of about 2 to 1). There is no upper limit if it is assumed that  $y$  can vary infinitely. Obviously, there must be a limit to the number of water molecules that can be accommodated in the channel. Without going into this question, however, it is possible to calculate a probable upper limit for the density of zemannite and, further, to reduce the range in density.

The approach was to calculate the densities

of various compositions in two ways. First, the density was calculated in the usual way from the unit-cell parameters. Next, the density was calculated from the Gladstone-Dale relationship.

The formula used is  $\rho = \frac{\bar{n} - 1}{K}$ , where  $\rho$  is density,  $\bar{n}$  is the mean refractive index, and  $K$  is the specific refractive energy of the mineral. The mean refractive index for a uniaxial mineral such as zemannite is given by the formula,  $\bar{n} = \frac{2\omega + \epsilon}{3}$ . The value of  $K$  must be calculated

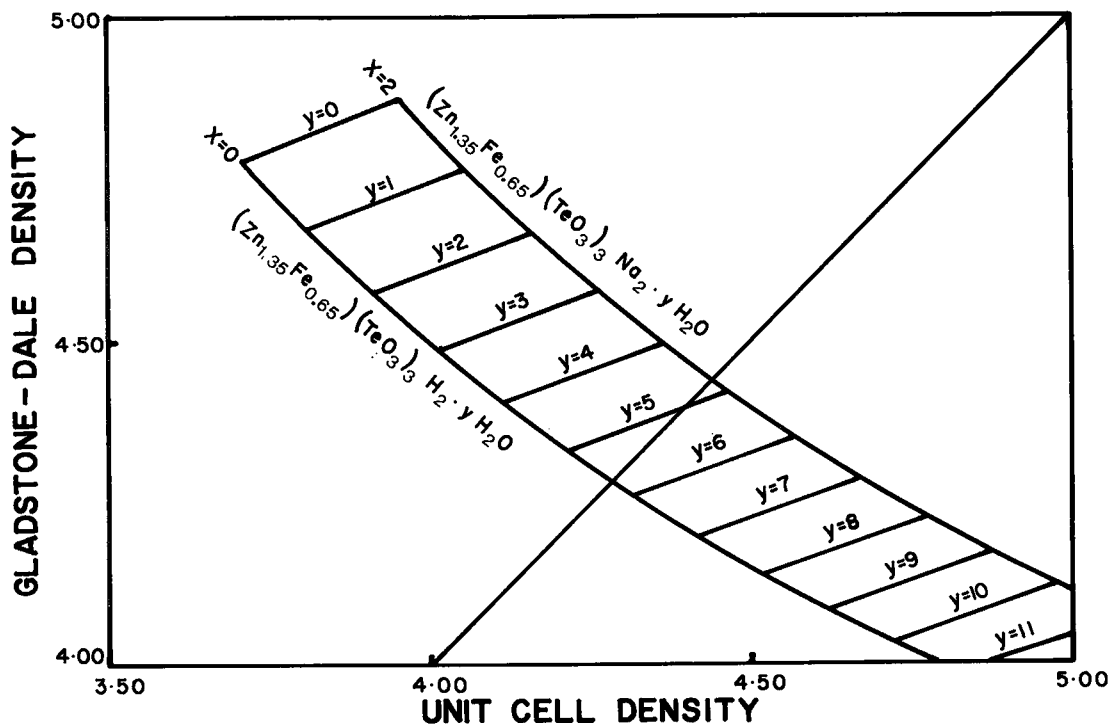


FIG. 2. Unit cell density versus Gladstone-Dale density of  $(Zn_{1.35}Fe_{0.65})(TeO_3)_3Na_2H_{2-x} \cdot yH_2O$ , for various values of  $x$  and  $y$ .

from the weight percentages of each constituent for a particular composition and from the specific refractive energies of those constituents. The formula for this relationship is:  $K = \frac{k_1 p_1}{100} + \frac{k_2 p_2}{100} + \dots + \frac{k_n p_n}{100}$ . Here,  $k_1, k_2, \dots$  etc. are the specific refractive energies of the constituents and  $p_1, p_2, \dots$  etc. are the weight percentages of the constituents. The values of the  $k$ 's used in these calculations are those given by Mandarino (1976). A sample calculation for an assumed composition of  $(Zn_{1.35}Fe_{0.65})(TeO_3)_3 NaH \cdot 5 H_2O$  is given in Table 2.

The values of the two densities were calculated for various compositions and are plotted against each other in Figure 2. The compositional limits of zemannite are represented by a band running from upper left to lower right. The width of the band is governed by the value of  $x$ . The length of the band is determined by the value of  $y$ . The line at  $45^\circ$  to the coordinates represents points where the "structural" densities are equal to the "Gladstone-Dale" densities. This line intersects the band at  $4.28 \text{ g/cm}^3$  and  $4.44 \text{ g/cm}^3$ . The density of zemannite is probably between these two values. The average of these values is  $4.36 \text{ g/cm}^3$ . In Figure 2, this density corresponds to a composition of  $(Zn,Fe)_2(TeO_3)_3 NaH \cdot 5.2 H_2O$ .

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