THE CHEMICAL FORMULA AND CRYSTAL SYSTEM OF ALLEGHANYITE*

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In looking over a thin-section of the alleghanyite-bearing vein from Bald Knob, Alleghany County, N. C., I was impressed with the resemblance of the subhedral crystals of alleghanyite to crystals of chondrodite in metamorphic limestones.

The formula $5MnO \cdot 2SiO_2$ was assigned to alleghanyite by Ross and Kerr.[1] The formula of chondrodite is $5MgO \cdot 2SiO_2 \cdot H_2O$ for the fluorine-free end member. It then occurred to me that the water content of alleghanyite might have been overlooked in the original analysis. Such proves to be the case, for a good closed tube test for water was obtained from the alleghanyite. It seemed reasonable, then, that alleghanyite might be the manganese analogue of chondrodite with the formula $5MnO \cdot 2SiO_2 \cdot H_2O$ or $2Mn_2SiO_4 \cdot Mn(OH,F)_2$. A new analysis has been made and the mineral has been carefully examined in thin-sections. As a result of this study I am convinced that the formula of alleghanyite is $5MnO \cdot 2SiO_2 \cdot H_2O$ and not $5\ MnO \cdot 2SiO_2$ as given by Ross and Kerr. Ross and Kerr went to great pains to show that alleghanyite is not tephroite ($2MnO_2 \cdot SiO_2$), but overlooked its possible relation to other mineral groups.

As will be seen later, alleghanyite is monoclinic and not orthorhombic as Ross and Kerr state.

The specimens on which this study is based were kindly furnished me by Dr. D. F. Hewett of the United States Geological Survey, who collected them at the original locality.

Specimens of the alleghanyite-bearing vein have a banded gneissoid appearance with colorless manganian calcite and reddish alleghanyite. Small black submetallic grains prove to be galaxite. Thin-sections show a small amount of alabandite, a mineral which was overlooked by Ross and Kerr. The alabandite is translucent green in thin fragments and is optically isotropic. It is soluble in hydrochloric acid with the evolution of hydrogen sulfide. The alabandite is readily distinguished from galaxite in thin-sections when examined in reflected light. As noted by Hewett and Rove,[2] ala-

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[1] *American Mineralogist*, vol. **17**, pp. 9–10, 1932.

[2] *Economic Geology*, vol. **25**, pp. 36–56, 1930.

bandite is a widely-distributed mineral in manganese deposits, but has often been overlooked.

Geometrical Crystallography

The alleghanyite occurs in small (usually between 0.3 and 1 mm.) subhedral crystals which are ordinarily somewhat rounded. Most of the crystals are equidimensional with a tendency toward tabular habit (see Figs. 3 and 5). If the alleghanyite is the manganese analogue of chondrodite then the dominant form of many crystals is {001}. It is common to find crystal sections with one well-defined straight edge (see Figs. 3–6). This is the trace of the (001) face. There is occasionally an imperfect cleavage (or parting) trace parallel to this face (see Fig. 3, upper right center).

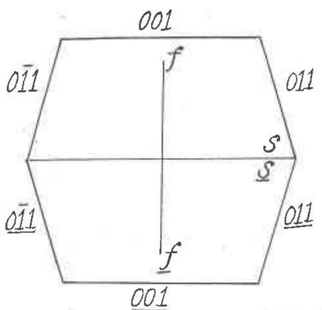

Fig. 1. Section of twinned alleghanyite cut parallel to (100). (f=fast ray; s=slow ray.)

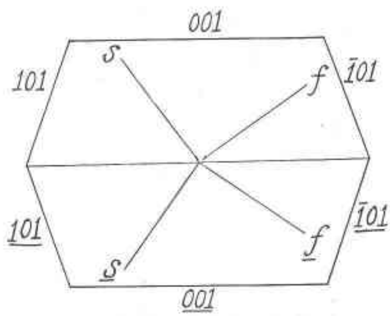

Fig. 2. Section of twinned alleghanyite cut parallel to (010).

Careful search of thin-sections reveals a few sections of euhedral crystals on which approximate measurements have been made. Four or five sections essentially like Fig. 1 were noted. This is interpreted as a section approximately parallel to (100), since it gives parallel extinction to the trace of (001) with the slow ray in the horizontal position. The outlines of the section are traces of the (001), (011), and (0$\bar{1}$1) faces. The angle (001 $\wedge$011) varies from 73 to 75°. The corresponding angle for chondrodite is $72°21\frac{1}{2}'$. All but one of the measured (100) sections are twins with (001) as the twin-plane. It is possible that in the crystals with sections like Fig. 1 the form present is {111} or even {*hll*} instead of {011}, but this would not change the value of the angle for this particular section. The interzonal angle [010] $\wedge$ [0$\bar{1}$1] is the same as the interfacial angle (001) $\wedge$(011).

One measurable section like Fig. 2 was found. This is a twinned crystal cut approximately parallel to (010), for the extinction angle is near the maximum value. The forms are evidently {001}, {101}, and {$\bar{1}$01}. The angle (001 $\wedge$101) is about 69°; the corresponding angle for chondrodite is 70°56½′.

The forms {001}, {011}, {101}, and {$\bar{1}$01} are very common for chondrodite and one would expect them to be common for the manganese analogue of chondrodite. The geometrical crystallography of alleghanyite as far as can be ascertained seems to be similar to that of chondrodite. Some of the common forms are the same and the interfacial angles are similar.

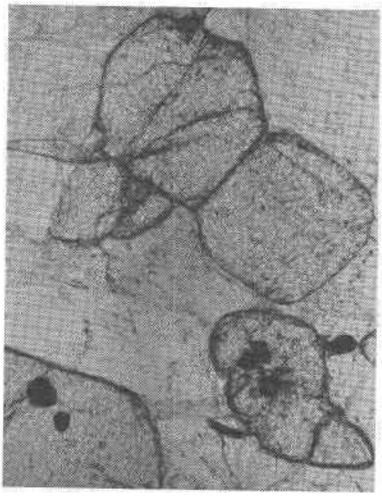

FIG. 3. (×56 diameters.) Subhedral crystals of alleghanyite in a matrix of calcite. The opaque mineral is galaxite.

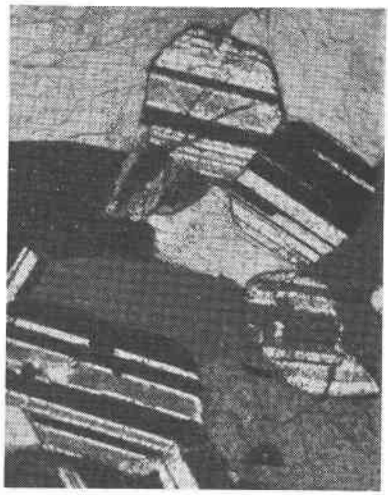

FIG. 4. (×52 diameters.) The same as Fig. 3, but taken with crossed nicols to show the polysynthetic twinning.

The symmetrical section shown in Fig. 2 seems to indicate that alleghanyite is orthorhombic but the oblique extinction proves it to be monoclinic. It will be recalled that chondrodite is unusual in that the angle β between the *a*- and *c*-axes is 90°. The probability is that β is also 90° or at least near 90° in alleghanyite.

A great majority of the alleghanyite crystals are twinned as was emphasized by Ross and Kerr. The twinning is usually polysynthetic, but frequently with only a few lamellae, often a single twin-seam. The twin-lamellae are broader and not as numerous as in the average plagioclase section. The twinning is remarkably like that shown in thin-sections of chondrodite; it was this observation that led to the discovery that alleghanyite is the manganese analogue of chondrodite. The twin-plane is taken as (001) to correspond to the common twin-plane of chondrodite. The photomicrographs of Figs. 4 and 6 give a good idea of the twinning in alleghanyite.

A few sections of peculiar composite twins of alleghanyite were observed. These are illustrated by Figs. 7 and 8. Only one of these sections is oriented so as to give an accurate measurement of interfacial angles but there seems to be no doubt as to their interpretation. In each of these, two different twin-laws are exemplified.

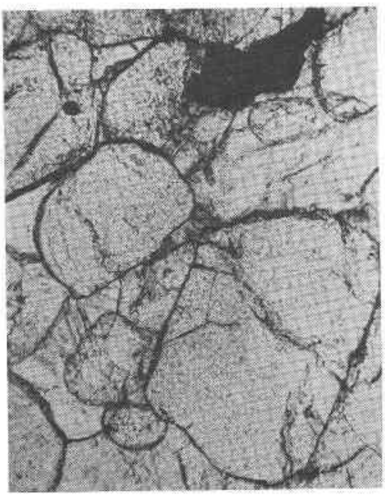

Fig. 5. (×56.) Subhedral crystals of alleghanyite with opaque galaxite.

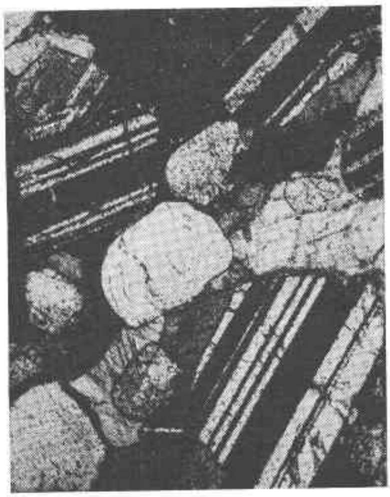

Fig. 6. (×52.) The same as Fig. 5, but taken with crossed nicols to show the polysynthetic twinning.

The polysynthetic twinning in each case is parallel to {001}. In Fig. 7 the reëntrant twinning is (105). The angle $(001 \wedge \underline{001})$ is about 61°; the calculated angle for chondrodite twinned on (105) is 60°8′ (2×30°4′, since $001 \wedge 105 = 30°4'$). The extinction angle in the section is about 35°, which is the maximum for alleghanyite; hence the section is parallel to (010). The section shown in Fig. 8 is equally inclined to the twin-plane but it is not parallel to (010), as the extinction angle is only 20°. The angle $(001 \wedge \underline{001})$ is equal to about 68°. In this section the twin-plane must be (305). The calculated interfacial angle $(001 \wedge \underline{001})$ for chondrodite twinned on

(305) is 59°52′. The divergence in value of this angle is due to the fact that the section is not parallel to (010).

Twins with (105) and (305) as twin-planes combined with polysynthetic (001) twinning are very characteristic of chondrodite.[3,4] The presence of twinning according to the three twin-laws (001), (105), and (305) known for chondrodite, on alleghanyite is strong corroboration of the view that alleghanyite is the manganese analogue of chondrodite.

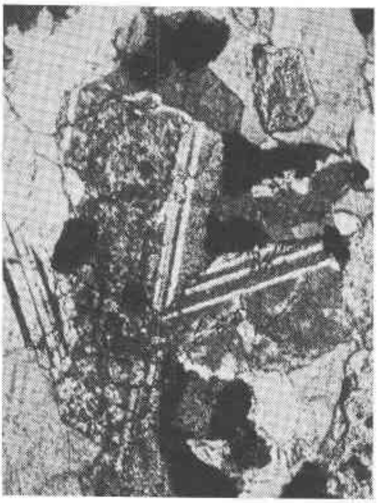

Fig. 7. (×56.) Composite twin of alleghanyite taken with crossed nicols. The twin-planes are (001) and (105).

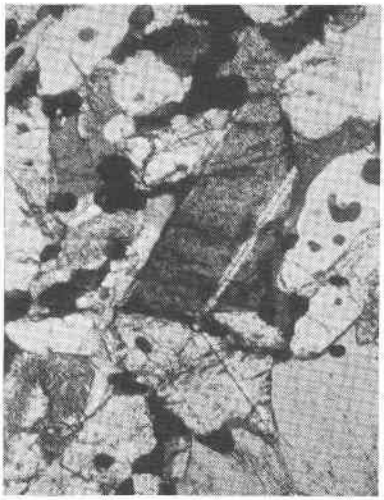

Fig. 8. (×56.) Composite twin of alleghanyite taken with crossed nicols. The twin-planes are (001) and (305).

In twins of chondrodite, twin-laws according to (105) and (305) are often difficult to distinguish from each other, but in this particular case it is easy to make the distinction on account of the presence of polysynthetic (001) twinning.

Structural Crystallography

Powder photographs of alleghanyite were kindly made for me by my colleague, Dr. J. L. Hoard of the Chemistry Department, and, for comparison, also powder photographs of chondrodite from

[3] See Rosenbusch-Mügge, *Mikroskopische Physiographie der petrographisch-wichtigen Mineralien*, Band **I**, 2d Hälfte, p. 445, *Stuttgart*, 1927.

[4] See also Goldschmidt, *Atlas der Krystallformen*, Band **IV**, Tafel 103, Fig. 103, *Heidelberg*, 1918.

the Tilly Foster mine, Brewster, N. Y. The chondrodite is a massive yellow-brown mineral associated with cleavable dolomite, chlorite, and magnetite. Diffraction patterns of the two minerals are shown side by side in Figs. 9 and 10. There is distinct similarity in the two patterns, which points to some relation between the alleghanyite and chondrodite.

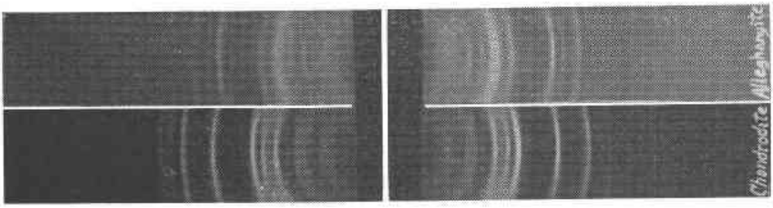

FIG. 9. (upper). Diffraction pattern of alleghanyite.
FIG. 10. (lower). Diffraction pattern of chondrodite.

For some of the better defined lines of the alleghanyite pattern there are corresponding lines in the chondrodite pattern. In order to prove this statement the following tabulation is presented:

THE DISTANCE D IN MILLIMETERS FROM THE ZERO BEAM OF SOME OF THE LINES OF AN ENLARGED POWDER PHOTOGRAPH

No.[5]	For Alleghanyite	For Chondrodite	Difference
5	24.1	27.5	3.4
8	28.0	29.5	1.5
10	29.4	30.9	1.5
11	31.8	32.2	0.4
15	42.1	43.5	1.4
16	43.5	45.1	1.6
17	45.0	47.5	2.5
18	47.0	49.0	2.0
19	49.0	51.3	2.3
21	52.1	54.6	2.5
23	54.0	56.8	2.8
25	69.8	71.5	1.7
			Ave. = 1.96

The similarity is perhaps not great enough to prove that the two samples used for the photographs are isomorphous. It is likely that the Tilly Foster specimen is not chondrodite, but another member

[5] The first column gives the arbitrary numbers of Ross and Kerr.

of the humite group. The diffraction patterns indicate that alleghanyite is related to the humite group in some way. The chemical analysis given later proves that alleghanyite is isomorphous with chondrodite.

Ross and Kerr point out the close similiarity of the diffraction patterns of alleghanyite and tephroite. Now there is a reasonable explanation of this similarity and of the practical identity of some of the lines. Taylor and West[6] have shown that chondrodite is made up of double layers of Mg_2SiO_4 alternating with one layer of $Mg(OH,F)_2$. So that if tephroite bears the same relation to alleghanyite that forsterite does to chondrodite, as seems probable, one would expect the diffraction pattern of alleghanyite to be similar to that of tephroite.

Optical Crystallography

Most of the subhedral alleghanyite crystals show polysynthetic twinning when examined in thin-sections between crossed nicols (see Figs. 4 and 6). The twin-plane is (001) since alleghanyite is in all probability isomorphous with chondrodite. Some sections give a negative optic-axis interference figure with a rather large axial angle.[7]

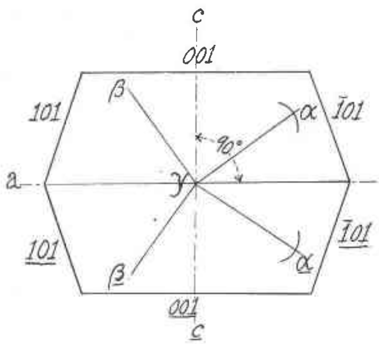

Fig. 11. Optical orientation of alleghanyite. This represents a twinned crystal cut parallel to (010). $a \wedge \alpha = -35°$, $b = \gamma$, $c \wedge \beta = -35°$. Axial plane $\perp$ (010). Optic sign (−).

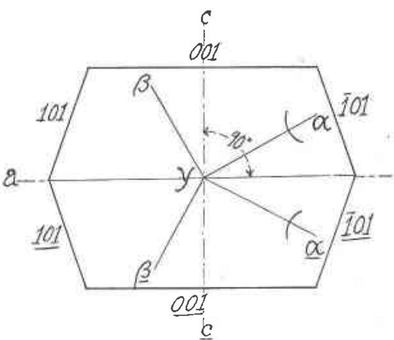

Fig. 12. Optical orientation of chondrodite. This represents a twinned crystal cut parallel to (010), $a \wedge \alpha = -26$ to $-31°$, $b = \gamma$, $c \wedge \beta = -26$ to $-31°$. Axial plane $\perp$ (010). Optic sign (+).

Most of the twinned sections show oblique extinction and the maximum extinction angle measured from the trace of the twin-

[6] *Proc. Roy. Soc.* (*London*), vol. **117A**, pp. 517–532, 1928.

[7] According to Ross and Kerr, 2V = 72°.

plane (001) is about 35°. Ross and Kerr give this angle as 22°, but in various sections many values higher than 22° were found, with the maximum at 35°. The extinction direction 35° from the trace of (001) is the faster ray. Other sections twinned on (001) have parallel or nearly parallel extinction with the trace of the twin-plane parallel to the slower ray. The optical orientation of alleghanyite, then, is as shown in Fig. 11. This is similar to the optical orientation of chondrodite (Fig. 12) except that the latter mineral is optically positive.

The optical properties prove beyond any doubt that alleghanyite is monoclinic and not orthorhombic. The statement of Ross and

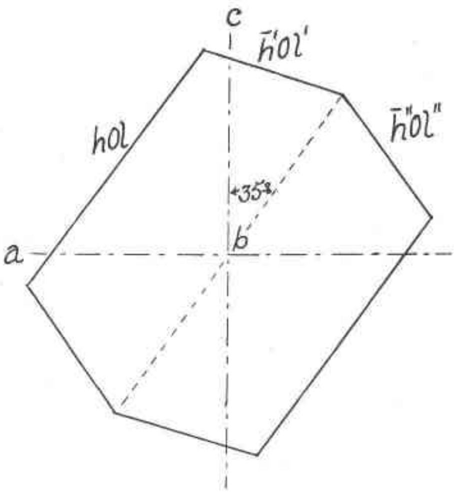

Fig. 13. The geometrical orientation of alleghanyite provided it is orthorhombic.

Kerr, "The bilateral symmetry of the twinning in two perpendicular planes indicates that the mineral [alleghanyite] is orthorhombic," is not at all convincing. If alleghanyite is orthorhombic, the geometrical orientation would have to be something like that shown in Fig. 13. The combination of forms would be $\{h0l\}$, $\{\bar{h}'0l'\}$ and $\{\bar{h}''0l''\}$ as given in the figure. The axes of reference must be parallel to extinction directions and if the mineral is orthorhombic they must either all be axes of 2-fold symmetry or there must be two planes of symmetry with a 2-fold axis at their intersection. It is clear, therefore, that alleghanyite cannot belong to any of the three crystal classes of the orthorhombic system.

Chemical Composition

In view of my belief that the chemical formula of alleghanyite is different from the one given by Ross and Kerr, I thought it advisable to have a new chemical analysis made. Accordingly, a sample was prepared by a combination of hand picking, electromagnetic separation,[8] and separation by Clerici solution. The sample was not quite pure, but contained small amounts of calcite and galaxite with a little alabandite.

The analysis was made by Dr. R. B. Ellestad of the Rock Analysis Laboratory of the University of Minnesota with the following results (column I):

	I	II	Galaxite	Calcite	Alabandite	Alleghanyite	
SiO_2	22.75	.3732				3732	3750
TiO_2	0.15	.0018				18	
Al_2O_3	0.75	.0073	73				
Fe_2O_3	0.73	.0046	46				
CaO	1.34	.0239		239			
MgO	0.71	.0176				176	9399
MnO	67.85	.9566	46..73	197	27	9223	
H_2O	2.56	.1422				≏(OH) 2841	2998
F	0.30	.0157				157	
CO_2	1.92	.0436		239..197			
S	0.11	.0021			21		
	99.17						
Less O≏F+S=	0.35						
Total	98.82						

The molecular ratios are given in column II. Assuming the formula of galaxite to be $Mn(Al,Fe)_2O_4$, all the alumina and ferric oxide and equivalent amounts of manganous oxide are assigned to galaxite. The sulfur is allotted to alabandite. All the lime and an amount of manganous oxide equivalent to the rest of the carbon dioxide is assigned to the manganian calcite. The remainder of the manganous oxide plus the magnesia is left for alleghanyite. The titania[9] is combined with the silica. The water is calculated as hydroxyl in order that the fluorine may be combined with it.

The ratios, then, are 9399 MnO:3750 SiO_2:2998(OH,F). Since

[8] The galaxite has a greater magnetic susceptibility than alleghanyite.

[9] It will be recalled that the so-called "titanolivin" is a titanian clinohumite; it is therefore not surprising to find titanium in alleghanyite.

the formula of the manganese analogue of chondrodite is $4MnO \cdot 2SiO_2 \cdot Mn(OH,F)_2$ the ratios for alleghanyite may be expressed as: $7500MnO \cdot 3750SiO_2 \cdot 1470Mn \cdot 2998(OH,F)$, which is equivalent to $4(1875)MnO \cdot 2(1875)SiO_2 \cdot 1(1485)Mn(OH,F)_2$ or $4MnO \cdot 2SiO_2 \cdot 0.79Mn(OH,F)_2$.[10] This is very close to $4MnO \cdot 2SiO_2 \cdot 1Mn(OH,F)_2$. There is a slight deficiency of combined hydroxyl and fluorine, which is probably due to inaccuracy in the fluorine determination. It will be noted that the summation of the analysis is rather low.

This new analysis ($5MnO:2SiO_2$) confirms the $5MnO:2SiO_2$ ratio of the analyses given by Ross and Kerr. But the presence of water and fluorine in the mineral establishes the formula as $2Mn_2SiO_4 \cdot Mn(OH,F)_2$, which together with the crystallographic properties proves that alleghanyite is isomorphous with chondrodite. The theoretical composition of $2Mn_2SiO_4 \cdot Mn(OH)_2$ is $MnO = 71.90$, $SiO_2 = 24.45$, $H_2O = 3.65$; and for $2Mn_2SiO_4 \cdot MnF_2$ it is $MnO = 71.32$, $SiO_2 = 24.25$, $F = 7.62$; Total $= 103.21 - 3.21$ $(O \approx F) = 100.00$.

Summary of Observations

The various arguments in support of the view that alleghanyite is the manganese analogue of chondrodite may be summarized thus:

1. Alleghanyite is monoclinic with $\beta(a \wedge c)$ either equal or nearly equal to 90° and with observed forms the same as some of the common forms of chondrodite.

2. The polysynthetic twins after (001) and the composite twins after (001) and (105) and after (001) and (305) are remarkably like those of chondrodite. The three twin-laws [(001), (105), and (305)] known for chondrodite are also the twin-laws for alleghanyite.

3. The diffraction pattern of alleghanyite is remarkably similar to that of chondrodite (or other member of the humite group).

4. The diffraction pattern of alleghanyite is much like that of tephorite, as it should be, since the internal structures of the

[10] 1485 is the average of 1470 and one-half of 2998.

analogous pair of minerals, chondrodite and forsterite, have much in common.

5. The $5MnO:2SiO_2$ ratio of alleghanyite corresponds to the $5MgO:2SiO_2$ ratio of chondrodite.

6. A small amount of titania recalls the existence of titanium-bearing clinohumite ("titanolivin").

7. The presence of water (hydroxyl) and fluorine in alleghanyite is matched by the presence of water and fluorine in chondrodite.

8. The ratios obtained from a new chemical analysis of alleghanyite agree better with the formula $2Mn_2SiO_4 \cdot Mn(OH,F)_2$ than they do with any other formula.

In view of the foregoing facts, there seems to be no doubt that alleghanyite is a monoclinic mineral with the formula $2Mn_2SiO_4 \cdot Mn(OH,F)_2$ and hence is isomorphous with chondrodite, $2Mg_2SiO_4 \cdot Mg(OH,F)_2$.

Summary of Corrected Data for Alleghanyite

Formula: $2Mn_2SiO_4 \cdot Mn(OH,F)_2$
Sp. Gr.: 4.020
Crystal system: Monoclinic; $\angle\beta=$ or $ca.=90°$
Forms: $\{001\}$, $\{011\}$, $\{101\}$, $\{\bar{1}01\}$
Twin-Laws: $\{001\}$, $\{105\}$, $\{305\}$
Indices of Refraction: $n_\alpha=1.756$, $n_\beta=1.780$, $n_\gamma=1.792$
Birefringence: $n_\gamma-n_\alpha=0.036$
Optical Character: $(-)$
Optic Axial Angle: $2V=72°$
Optical Orientation: $a \wedge \alpha=-35°$, $b=\gamma$, $c \wedge \beta=-35°$
Optic Axial Plane: $\perp(010)$.