

## STRUCTURES OF SULFIDES AND SULFOSALTS

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### INTRODUCTION

Mineralogists who look forward to simple and definite chemical formulas of minerals based on a knowledge of their structures will see their expectations only partly fulfilled. It is now well known that probably only organic crystals (including solid  $\text{CO}_2$  and  $\text{NH}_3$ ) possess definite molecules, while in inorganic solids the molecule as such does not seem to exist. A few possible exceptions may include very complex compounds like the micas (1). The sulfides and sulfosalts whose structures have been determined do not show definite combinations of atoms that could be designated as molecules. Some seem to contain distinguishable radicals, however, if  $\text{S}_2$  in pyrite, for example, may be considered a radical.

In the following pages the different types of sulfides and sulfosalts including several artificial compounds will be discussed and interesting similarities will be pointed out. Many tellurides and selenides have the same structures as the corresponding sulfides but they will not be mentioned here. Whether the particles composing the structures are in the atomic or ionic state is still doubtful. Reference to this subject will be made only in two or three groups enumerated. It is impossible to give all the references to the original investigations of the structures described. Ewald's and Herrmann's volume "Strukturbericht" (2) contains most of these, and frequent reference will be made to this compilation.

### SULFIDES

**NaCl STRUCTURE TYPE:** Galena,  $\text{PbS}$ ,  $\text{MgS}$ ,  $\text{CaS}$ ,  $\text{SrS}$ ,  $\text{BaS}$  and alabandite,  $\text{MnS}$ , crystallize like  $\text{NaCl}$  (2, p. 72), see Fig. 5 in this journal,<sup>1</sup> page 183. If we imagine the S atoms to be connected which are nearest to one another we notice that each group of four forms a regular tetrahedron. A whole net work of tetrahedrons is obtained in this way. These S atoms have the so-called cannon ball arrangement designated by W. H. and W. L. Bragg as face-centered cubic close packing (3, p. 161). Spheres of equal radius which touch when arranged in this manner occupy the smallest possible space. It seems to be a very common packing of oxygen in oxides and silicates according to Bragg and other investiga-

<sup>1</sup> In order to avoid repetition of drawings, reference will be made to the figures in the paper "Crystal structure types," this journal, vol. 14, pp. 182-187, 1929.

tors. In the structures under discussion the S atoms cannot touch one another because the metal atoms are also arranged in the same pattern and their tetrahedrons interpenetrate the S tetrahedrons. It depends on the size of the metal atom as to how close the S atoms can approach each other. The length of the edge of the S tetrahedron in PbS, for example, is 4.19Å while in MnS it is 3.68Å. If we compare the measured dimensions of the unit cells of these sulfides with those computed from the atomic and ionic radii of Goldschmidt (4) we find that the ionic ones are in better agreement than the atomic ones. Whether this means that the particles are ions (making the lattices polar) or not, is not apparent, for in all the remaining structures discussed below the *atomic* radii agree better, or just as well, as the ionic radii with the measured dimensions.

A noteworthy feature is that the natural minerals crystallizing with NaCl structure, NaCl, PbS, MnS, MgO, PbSe, PbTe, MnO, have cubic cleavage. Exceptions are AgCl, AgBr and AgI which have no cleavage at all.

ZINCBLENDE STRUCTURE TYPE: BeS, zinblende, ZnS, (including the iron rich marmatite and christophite), artificial CdS, and black HgS crystallize in this type (2, p. 76). To illustrate this type see this journal, vol. 14, p. 185, Fig. 8. The S atoms as well as the metal atoms form regular tetrahedrons in such a way that one half of the tetrahedrons of one element have an atom of opposite charge in their centers. The radius of the metal atom in the center of the S tetrahedron determines its size. Since the S atoms as well as the metal atoms, viewed independently, form face-centered cubes they have the same close packing arrangement observed in NaCl structures. As was pointed out by Goldschmidt (4, p. 75) the atomic radii when used to compute the theoretical dimensions of the zinblende structure agree much better with the measured values than the ionic ones, a fact which has led some investigators to believe that this lattice may be an atomic (non-polar or homoeopolar) one.

WURTZITE STRUCTURE TYPE: Only two sulfides, wurtzite, MnS, and greenockite, CdS, belong to this hexagonal type. A diagram of this structure is shown in this journal, vol. 14, p. 185, Fig. 9. It resembles zinblende in the following respects:

1. The distances between the atoms are practically identical to those in zinblende.

2. A rotation of 60 degrees of *alternate pairs* of (0001) atomic layers about the three fold axis produces the zinblende structure.

3. The S as well as the metal atoms form interlocking tetrahedrons. Since the axial ratio  $c/a$  in wurtzite is almost exactly 1.633 (which is twice the ratio of the height of a regular tetrahedron to its edge) the tetrahedrons are practically regular. The same is true of CdS.

4. The arrangement of the S as well as the metal atoms—each one viewed independently—is that of hexagonal close packing. This as pointed out by Bragg (3, p. 161) is the alternative of close packing and produces just as dense a structure as the face-centered cubic packing, provided the hexagonal axial ratio  $c/a$  is 1.633.

**NIAS STRUCTURE TYPE:** Pyrrhotite, FeS, artificial NiS (not millerite), and CoS belong to this hexagonal type (2, p. 84). See this journal, vol. 14, p. 183, Fig. 6. Only the S atoms have the positions of hexagonal close-packing as discussed for wurtzite. However since the axial ratios  $c/a$  are 1.688, 1.55 and 1.52, respectively, the packing is not as close. Again the S atoms form almost regular tetrahedrons which, however, do not contain any metal atoms. Each metal atom is surrounded by 6 S atoms which are at the corners of a slightly distorted octahedron.

No structural reason for the easy replacement of Fe by S in pyrrhotite can be given, unless it is the tendency for the S atoms to form radicals similar to S-S, as found in pyrite. In pyrrhotite replacement of Fe by S would bring certain S atoms as close together as 2.45Å, while in the theoretical pyrrhotite structure the S atoms are separated by at least 3.43Å. The S atoms in the pyrite radical (See Fig. 1) are only 2.09Å apart which is closer than in any other determined sulfide.

**CINNABAR:** Cinnabar, HgS, is hexagonal but it resembles a distorted NaCl structure (2, p. 88). Therefore, one may apply what has been said concerning PbS provided the distortion of the lattice is not left out of consideration.

**FLUORITE STRUCTURE TYPE:** The cubic chalcocite,  $\text{Cu}_2\text{S}$ ,  $\text{Na}_2\text{S}$ , and  $\text{Li}_2\text{S}$  belong to this type (2, p. 148). A diagram of the structure is given in this journal, vol. 14, p. 185, Fig. 11. The S atoms occupy the Ca positions in fluorite while the metal atoms occupy those of F. For this reason Goldschmidt refers these structures to the "anti-fluorite" type. The S atoms are arranged in face-centered cubic close packing and form, therefore, regular tetrahedrons. Each tetrahedron contains one metal atom. The metal atoms are arranged in small cubes.

PYRITE STRUCTURE TYPE: Pyrite,  $\text{FeS}_2$ , hauerite,  $\text{MnS}_2$ ,  $\text{CoS}_2$ , and  $\text{NiS}_2$  crystallize in this type (2, p. 150). Cobaltite,  $\text{CoAsS}$ , gersdorffite,  $\text{NiAsS}$ , and ullmannite,  $\text{NiSbS}$ , have very similar structures. One of the S atoms of the S-S radical might be considered as being replaced by As or Sb. In pyrite the metal atoms have face-centered cubic arrangement as shown in Fig. 1. Each metal

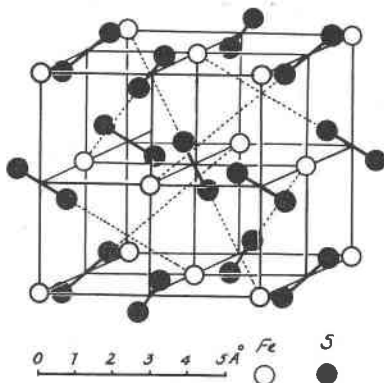
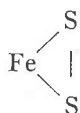


Fig. 1. Unit cube of pyrites. The dotted lines are threefold axes of symmetry.

atom is surrounded by a somewhat distorted inclined octahedron of six S atoms. The arrangement is similar to pyrrhotite in that respect. In pyrite we encounter a S-S radical and therefore Niggli writes the formula as:



The two S atoms of the radical are only 2.09 Å apart. The radicals might be compared to dumb-bells whose axes are parallel to the threefold cubic axes. The radicals are distributed in such a manner that each octant of the unit cube contains half a radical. But the axes of adjoining radicals (which are less than the length of the edge of the unit cube apart) are not parallel as may be seen in Fig. 1. Each S atom of the radical forms the corner of three tetrahedrons which are symmetrical with respect to the threefold axis in which the radical lies. These slightly distorted tetrahedrons are linked to other sets of tetrahedrons directly, as well as by means of the radicals. It is not feasible to show this arrangement in a two dimensional diagram. The centers of gravity of the "dumb-bells"

are in the positions of face-centered cubes, and, therefore, the *radicals* are in close packing. This gives a very dense structure for pyrite as seen by a comparison with zincblende whose unit cell has practically the same size. Each cell contains four molecules but pyrite has twice as many S atoms in the same volume.

**MOLYBDENITE STRUCTURE TYPE:** Molybdenite,  $\text{MoS}_2$ ,  $\text{WS}_2$  and probably  $\text{TiS}_2$  (9) crystallize in the hexagonal layer lattice type (2, p. 164). See this journal, vol. 14, p. 187, Fig. 17. These structures seem to be the result of the great deforming influence of tetravalent metal atoms (5, p. 180). The metal atoms are arranged in layers parallel to the base. Sets of two equivalent layers of S atoms are placed between the metal layers. The S atoms form layers of trigonal pyramids which are 3.66Å (3.63Å in  $\text{WS}_2$ ) in length along the pyramid edges and 3.15Å (3.18Å in  $\text{WS}_2$ ) along the basal edges. One is tempted to compare these pyramids with somewhat stretched tetrahedrons the elongation being due to the deforming influence of the metal atoms. The good basal cleavage in these compounds shows that the bonds between the S layers are relatively weak.

#### SULFOSALTS

There seems to be no general agreement among chemists and mineralogists as to what constitutes a sulfosalt. Some restrict the term to salts of hypothetical sulfoacids of V, As, Sb, and Bi. Others include sulfoferrites, as for example chalcopyrite and bornite. The writer believes the latter course the more logical one. Structurally there is little if any evidence that, for example, tetrahedrite resembles more closely a sulfosalt than does chalcopyrite. As a matter of fact they are surprisingly similar as will be shown later. Distinct radicals are no more frequent (as far as we know now) among the sulfosalts than among the sulfides. It will be shown, however, that those minerals which are classed as sulfosalts by the writer have at least two positions which are not equivalent structurally for the two or more metals. The Fe atoms in chalcopyrite, for example do not occupy interchangeable positions with Cu. Or in linnaeite  $(\text{Co}, \text{Ni})_3\text{S}_4$  the Co and Ni positions are structurally not the same or equivalent. The formula should be written  $\text{CoNi}_2\text{S}_4$  or  $\text{NiCo}_2\text{S}_4$ . In this case, as in most sulfosalts, isomorphous replacement is a prominent feature and a Co atom may take the place of a Ni atom or vice versa. But if it does, the new position which the Co fills remains a Ni position structurally.

The writer would suggest, therefore, that a salt in order to be considered a sulfosalt must have at least two structurally non-equivalent positions for its two or more metals.

**CHALCOPYRITE:** The structure of chalcopyrite,  $\text{CuFeS}_2$ , is represented by Fig. 10, this journal, vol. 14, p. 185. The arrangement of the S atoms in tetrahedral close-packed fashion is very similar to that in zincblende. As a matter of fact the structure as a whole (2, p. 279) is like zincblende if we disregard its tetragonal character, which is due to the fact that only alternate metal layers that are parallel to the base consist of the same metal, and

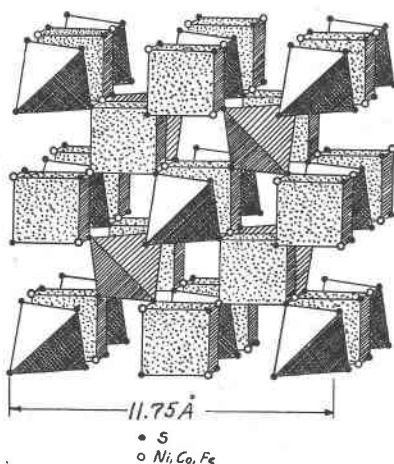


FIG. 2. Arrangement of tetrahedrons in linnæite (magnetite type). Each small cube also consists of a S tetrahedron and an interpenetrating metal. Each tetrahedron (not those in the cubes) contains a metal atom at its center. The eight atoms in the centers of the tetrahedrons at the corners of the drawing are the corners of a unit cube of linnæite. (After Ewald and Hermann.)

that the Fe positions are structurally not equivalent to the Cu positions.

**STANNITE:** Stannite,  $\text{Cu}_2\text{SnFeS}_4$ , is very closely related to chalcopyrite (2, p. 291). Though the S positions have not been determined with certainty it may be predicted that they resemble those of chalcopyrite. The three metals occupy positions which are not equivalent.

**MAGNETITE STRUCTURE TYPE:** Linnæite,  $(\text{Co}, \text{Ni})_3\text{S}_4$ , polydymite,  $(\text{Ni}, \text{Fe}, \text{Co})_4\text{S}_5$ , and sychnodymite,  $(\text{Co}, \text{Cu}, \text{Ni})_4\text{S}_5$ , crystallize in this type (8). Fig. 2 is a diagram of the structure. The 32 S

atoms (occupying the O positions of magnetite) form a tetrahedral net work of face-centered close-packed particles. Since the metals Co, Ni, Fe and Cu are very similar in radius and mass it is not known which metals occupy the 16 positions corresponding to ferric iron in magnetite and which the 8 ferrous positions. There is also considerable isomorphous replacement.

It will be noticed that the ratio of metal to S is 4:5 in polydymite and synchodymite. This is not such a serious objection, however. Translated into atoms of the unit cell it means 25.6:32, instead of 24 of the metal to 32 of S. This discrepancy might be explained in several ways. Submicroscopic impurities could be responsible. It is also conceivable that a metal atom takes the place of a S atom which would be the reverse of what happens in

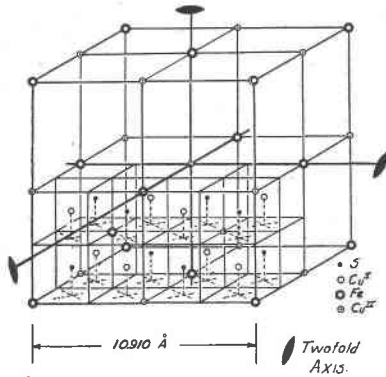


FIG. 3. Unit cube of bornite. The vacant octants may be filled by rotations about the twofold axes. (After DeJong.)

pyrrhotite. It has also been suggested that atoms may enter a structure without any definite positions of symmetry. This explanation is I believe too vague and should not be used till proof can be produced.

**BORNITE:** DeJong (6) has determined the structure of bornite. Its theoretical formula is  $\text{Cu}_5\text{FeS}_4$ . Of the 40 Cu atoms (or ions) in the unit cell, Fig. 3, 32 are cuprous and 8 cupric. The 32 S atoms have the same arrangement as in linnaeite. Therefore, they are face-centered close-packed. The 32  $\text{Cu}^{\text{I}}$  atoms are arranged in the same manner and their tetrahedrons bear the same relationship to those of the S atoms that a positive tetrahedron does to a negative one. A small discrepancy of less than 3 per cent of the parameter

of the  $\text{Cu}^{\text{I}}$  atom may be disregarded in this discussion. The structure of these 64 atoms closely resembles that of  $\text{PbS}$  ( $\text{NaCl}$  type). The eight  $\text{Cu}^{\text{II}}$  and eight  $\text{Fe}^{\text{II}}$  atoms are placed in the centers of some of the tetrahedrons of  $\text{S}$  and  $\text{Cu}^{\text{I}}$ . To account for the variable composition of bornite, from  $\text{Cu}_6\text{Fe}_2\text{S}_6$  to  $\text{Cu}_{18}\text{Fe}_2\text{S}_{12}$ , it is only necessary to imagine an isomorphous replacement of  $\text{Fe}^{\text{II}}$  by  $\text{Cu}^{\text{II}}$  atoms or vice versa. These two types of atoms have very similar positions, comparable in that respect to positive and negative tetrahedrons. Partial replacement, therefore, should be common.

**PENTLANDITE:** This mineral  $(\text{Fe},\text{Ni})\text{S}$  has been considered a sulfide but its structure (7) suggests a sulfosalt to the writer. Its formula should be written  $(\text{Ni}, \text{Fe})_3\text{FeS}_4$ . Theoretically it is  $\text{Ni}_3\text{FeS}_4$ . The  $\text{S}$  atoms are crowded into clusters of eight each. See Fig. 4. These eight form the corners of a small cube with an edge

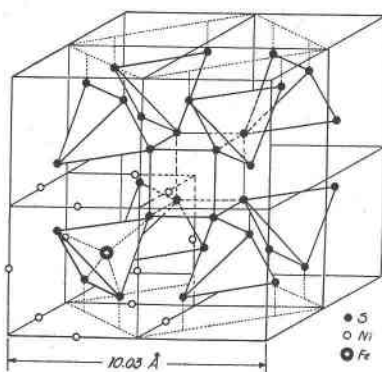


FIG. 4. Unit cube of pentlandite. Since the positions of the metal atoms are the same in all octants they have been shown in only one.

2.50 Å in length. This arrangement causes 8  $\text{S}$  atoms to occupy a smaller volume than in any other mineral combination known. These cubes of  $\text{S}$  are linked in such a manner that the corners of each four adjoining cubes form tetrahedrons of  $\text{S}$ . Each tetrahedron contains an  $\text{Fe}$  atom at its center. This  $\text{Fe}$  atom together with three  $\text{Ni}$  atoms (which by themselves form an equilateral triangle) are arranged in tetrahedral fashion. A unit cube of this structure contains 24  $\text{Ni}$ , 8  $\text{Fe}$  and 32  $\text{S}$  positions. Due to the peculiar distribution of the  $\text{S}$  atoms there appear to be "holes" in the structure.



**SULVANITE:** Sulvanite  $\text{Cu}_3\text{VS}_4$  is supposed to belong to the enargite group. DeJong who recently published its structure (10) places it in the cubic system. The S atoms in the structure are identical in arrangement to those of pentlandite (Fig. 4) and show, therefore, the same crowding. The V atoms have the same positions as the Fe in pentlandite. The Cu atoms surround each V atom in the form of an octahedron as shown in Fig. 5.

**TETRAHEDRITE:** The structure of this much discussed mineral is now known. DeJong (6) used the formula  $(\text{Cu}, \text{Ag})_3\text{SbS}_4$  in attempting to determine the structure, but Machatschki (11) has shown that this formula and structure are not in agreement with

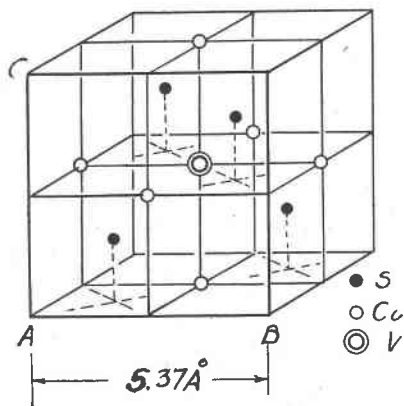


FIG. 5. An octant of a unit cube of sulvanite. All the faces of the octant are planes of symmetry. Reflection in them produces the other octants.

his own extensive investigation. The theoretical formula is  $\text{R}_3^{\text{I}} \text{R}^{\text{III}} \text{S}_3$ .  $\text{R}^{\text{I}}$  is chiefly  $\text{Cu}^{\text{I}}$  and  $\text{Ag}$  and  $\text{R}^{\text{III}}$  is  $\text{Sb}$  and  $\text{As}$ . A small excess of S is, however, very common which makes the working formula more often  $(\text{R}^{\text{I}}, \text{R}^{\text{II}})_{12} \text{R}_4^{\text{III}} \text{S}_{13}$ . There is no great difficulty in accommodating these extra S atoms in the structure.

The unit cell of tetrahedrite is very nearly eight times as large as that of chalcopyrite or sphalerite. One octant of the unit cube is shown in Fig. 6. The other octants result by rotation of the small cube about any of its edges as twofold axes. The structure resembles sphalerite or chalcopyrite, especially if the conventional point of origin O in Fig. 6 is shifted parallel to a threefold axis to the center A of the octant cube as pointed out by Machatschki (11). Then the 8 Sb positions lie almost at the corners of the resulting octant cubes

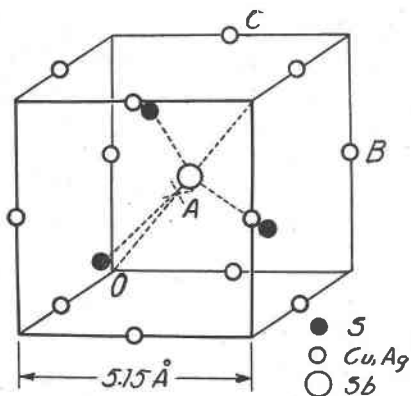


FIG. 6. An octant of a unit cube of tetrahedrite. The edges are twofold axes of symmetry. By their operation the other octants may be produced. The Sb atom is not in the center, A, of the octant but is displaced along the diagonal one eighth of the length of the diagonal of the octant.

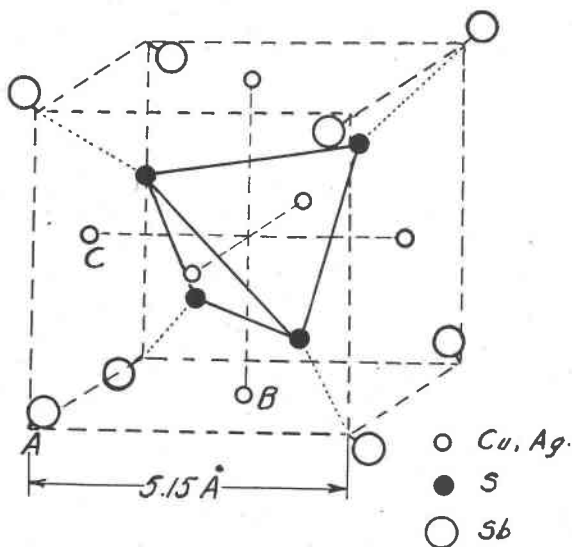


FIG. 7. Octant of tetrahedrite showing great similarity to the unit cell of chalcocpyrite and sphalerite. A shift from O to A in Fig. 6 produces the octant shown. Corresponding atoms in the two figures are designated by the same letters.

as shown in Fig. 7 in which the positions corresponding to those in Fig. 6 have been designated by the same letters. Each octant cube has almost the same dimensions as the unit cell of chalcocpyrite.

Also the arrangement of S and metal atoms is similar.

The metal atoms (including Sb) become face-centered for the octant cubes, and four S atoms, form tetrahedrons inside of the octant cubes (Fig. 7). But only six of the eight octant cubes contain these tetrahedrons. Two will be vacant, and it is in these that any excess S atoms over  $R_3^{I}R^{II}S_3$  are probably found (11, p. 209). Divalent metals like Zn and Fe can probably take some of the positions of Cu and Ag provided these additional S atoms are present.

### CONCLUSION

A comparison of the known structures of sulfides and sulfosalts shows the following important features.

1. Sulfosalts do not differ structurally from sulfides except the two or more metals in them occupy at least two structurally non-equivalent positions. This causes such minerals as pentlandite, for example, to come under the classification of sulfosalts.

2. Structural radicals are not distinguishable except in the pyrite group, pentlandite and sulvanite.

3. The most common arrangements of the S atoms in sulfides and sulfosalts seem to be those involving close packing of cubic face-centered (cannon ball fashion) and hexagonal types. It seems to the writer that slightly distorted close packing of this nature may also be expected in orthorhombic sulfides or sulfosalts. Oxygen atoms (or ions) also show these arrangements in many oxides and silicates as shown especially by W. L. Bragg.

4. With the exception of the layer lattices of the molybdenite group, most sulfides and sulfosalts have their S atoms arranged at the corners of regular or slightly distorted tetrahedrons. This necessarily follows in a close-packed structure. But S tetrahedrons also prevail in the other structures. The size of these tetrahedrons is determined by the radii of the metal atoms which are associated with them. The shortest tetrahedral edge seems to be in pyrite (3.09 Å), while in  $Na_2S$  the large radius of Na increases the length of the edge to 4.62 Å.

Though it is probable that future investigations may necessitate revisions of these conclusions it is hoped that the present non-mathematical comparative study will aid mineralogists in visualizing some of the combinations of structural units discovered in this large group of minerals.

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