

Germanate Zeolites: Contrasting the Behavior of Germanate and Silicate Structures Built from Cubic T_8O_{20} Units (T = Ge or Si)

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Abstract: A brief review of germanate-based zeolite-like structures is given. The frameworks of new germanates containing cubic Ge_8O_{20} clusters are analyzed in detail and compared with those of related silicates. It is shown that some topologies are suitable for silicates, but not for germanates; that others are suitable for germanates but not for silicates; and that a third class is suitable for both types of material.

Keywords: germanium • germanates • silicates • tetrahedral frameworks • zeolites

Introduction

The enormous importance, especially in the chemical industry, of the framework aluminosilicates^[1] has led to numerous studies of related systems. For example the isoelectronic substitution of $2Si \rightarrow Al + P$ has led to the discovery of a wide range of "ALPO" structures^[2] and related phosphate materials.^[3] Considerably less work has been done on tetrahedral frameworks with the congeners of Al and Si in the next row of the periodic table, namely, Ga and Ge (references below), and only recently have the first materials been prepared (ASU-7 and ASU-9) with a zeolite-like framework consisting entirely of tetrahedrally coordinated germanium.^[4] Our paper is largely concerned with them and what they teach us about constraints on possible new structures.

We are concerned mainly with four-connected tetrahedral framework structures, in which TX_4 tetrahedra share corners to produce a framework with stoichiometry TX_2 , as these

remain the most important single class of structures in this context. The prototype material is the quartz form of SiO_2 , and the corresponding quartz form of GeO_2 is well established. Both materials also have a cristobalite structure form in which the topology of the tetrahedral framework is different from that of quartz. The low-temperature form of GeO_2 has the six-coordinate rutile (TiO_2) structure and is also the structure of a high-pressure form of SiO_2 (stishovite); the idea of using Ge analogues as models for high-pressure silicates has a long history.^[5]

A major difference between tetrahedral silicate and germanate frameworks is that in the absence of constraints (this is the case in quartzes and cristobalites), the Si-O-Si and Al-O-Si angles are in a narrow range close to 145° , whereas the Ge-O-Ge and Ga-O-Ge angles are close to 130° . The importance of this difference is a major theme of this paper. In particular we show that structures constructed from T_8X_{20} units, with T atoms at the vertices of a cube, fall into three classes: those suitable for both germanates and silicates (they allow a range of possible T-X-T angles with regular tetrahedra), those suitable for silicates only (all T-X-T angles must be close to 145° if the tetrahedra are to be regular), and those suitable for germanates only (T-X-T angles required to be close to 130°). Observed silicates and germanates fit this pattern.

Germanate Zeolitic Materials

Although a review of aluminosilicate frameworks would require volumes, we can list the main structural studies of germanium-containing tetrahedral oxide frameworks. The most common naturally occurring framework structure is that of feldspar, which has compositions typified by $CaAl_2Si_2O_8$ and $NaAlSi_3O_8$, and Ge(Ga or Al) analogues such as $BaGa_2Ge_2O_8$ ^[6] and $NaAlGe_3O_8$ ^[7] are well established. $SrGa_2-Ge_2O_8$ ^[8,9] and $BaGa_2Ge_2O_8$ ^[8] have also been made with the related paracelsian framework.

The above are rather dense structures. A more open structure, often classed with the classical zeolites, is that of sodalite (framework composition $AlSiO_4$) and numerous germanate sodalites have been made with framework compositions such as $AlGeO_4$,^[10] $BeGeO_4$,^[11] $GaGe_5O_{12}$,^[12] and

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GaGe₂O₆.^[12] Some other germanium zeolite structures [references to the zeolite structures signified by a three-capital-letter code are to be found in the *Atlas of Zeolite Structure Types*^[13] with framework compositions are: analcime (ANA), ZnGe₃O₁₂^[14] and GaGe₂O₆;^[12] natrolite (NAT), Ga₂Ge₃O₁₀^[15] and AlGeO₄;^[16] cancrinite (CAN), AlGeO₄;^[17] DAF-2 (DFT), GaGeO₄ “UCSB-3”;^[12] gismondine (GIS), AlGeO₄;^[16] faujasite (FAU), AlGeO₄;^[16] and rho (RHO), AlGeO₄.^[16] Note that the evidence so far published for the last three consists only of X-ray diffraction powder patterns and that structural details are lacking.

A number of new framework structures were first or only made as germanates. These include the structure of KAlGeO₄ “d phase”^[18] found also in KCoPO₄,^[19] that of UCSB-7 found for framework compositions GaGeO₄, BeAsO₄, and ZnAsO₄,^[20] and GaGe₃O₈.^[12] UCSB-15 has a novel framework of composition GaGe₅O₁₅^[12] with five-membered rings, and UCSB-9 with framework composition Ga₂Ge₃O₁₀^[21] provides a rare example of a zeolite-like framework with three-membered rings.

Germanates with framework structures that contain six- (M), five- (M') and four-coordinate (T) Ge are also known. Perhaps the most studied has a framework composition M₄T₃O₁₂ and the cubic structure of the pharmacosiderite family of minerals (for which M = Fe or Al, T = As). A number of structures in which both M and T are Ge have been reported.^[22] A related Ge framework of composition MT₆O₁₅ with a one-dimensional pore system has also been described.^[23] Another related structure type has a framework composition MT₃O₉, the topology of wadeite (K₂ZrSi₃O₉), and can accommodate cations as large as Cs (as in Cs₂Ge₄O₉).^[24] These structures have rather small pores, which can admit, at most, one cation.

Related materials with slightly larger pores include one with framework composition M'T₅O₁₂ that accommodates tetramethyl ammonium, [Me₄N]⁺,^[25] and another with framework composition MM'₄T₄O₁₇(OH)₂ that incorporates the ethylene diamine dication, [H₃NCH₂CH₂NH₃]²⁺.^[26] Both these materials decompose when the occluded cations are removed by heating.

Recently our group has reported new germanate frameworks with four-, five-, and six-coordinate Ge atoms and that contain *exchangeable* organic bases. ASU-12^[27] with framework composition M₂M'₄T₈O₂₉F₄ contains [(CH₃)₂NH₂]⁺ and ASU-14^[28] with framework composition MM'₄T₄X₂₂ (X = O, OH) contains diprotonated piperazine, [HNC₄H₈NH]²⁺. ASU-12 is the first material of this class in which exchange of the organic template by inorganic cations has been demonstrated. We are excited by these developments which highlight the flexibility of germanium in adopting coordination numbers of 4–6 in contrast to Si, which is usually four-coordinate in oxides (an example of a compound with four- and six-coordinate Si is K₂Si₄O₉, which also has the wadeite structure).^[29] However, we feel that it would be premature to generalize about this class of materials until more experimental data, particularly structures, materialize. Instead in the remainder of this article we focus our attention on the new all-tetrahedral Ge frameworks of ASU-7 and ASU-9.

Structures Constructed from T₈X₂₀ Cubes

We start with the observation that both ASU-7 and ASU-9 contain cubic units of eight Ge atoms linked in a Ge₈O₂₀ cluster. In the zeolite jargon such a cube is referred to as a D4R (“double 4-ring”) unit. Such a T₈X₁₂X'₈ unit is illustrated in Figure 1. If it had the full symmetry of a cube ($m\bar{3}m = O_h$) and regular tetrahedra the T-X-T angle would be fixed at

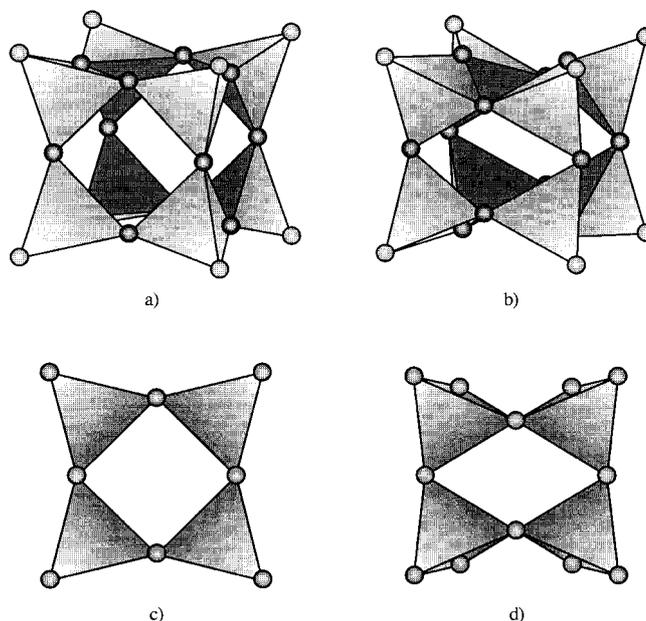


Figure 1. a) A T₈X₂₀ cluster with symmetry $m\bar{3}m$ and T-X-T = 148.4°. b) A T₈X₂₀ cluster with symmetry $m\bar{3}$ and T-X-T = 129.6°. c) and d) are projections of a) and b) down a fourfold or twofold axis, respectively.

$\cos^{-1}(-23/27) = 148.4^\circ$. We note in passing that even if two tetrahedra of different sizes (such as AlO₄ and PO₄ tetrahedra) alternated around the four-membered rings the T-X-T' angle in the highest symmetry configuration ($\bar{4}3m = T_d$) would remain the same.^[30] It is a nice coincidence that the T-X-T angle is close to the ideal value ($\approx 145^\circ$) for silicates, so it was a surprise to find that the cube was the building unit found^[4] in the first all-germanate zeolite-like structures.

The clue to understanding the occurrence of the unit in germanates is to realize that the T-X-T angle can be reduced while maintaining regular tetrahedra if the symmetry is reduced to $m\bar{3}$ (T_h) as also shown in Figure 1b. The transformation corresponds to rotation of the tetrahedra around three-fold axes. It is of considerable interest, in this context, that a careful study of the structures of a number of Si₈O₂₀ moieties showed that the small departures from octahedral symmetry corresponded very closely to motions of rigid tetrahedra of this sort.^[31] If the rotation is allowed to continue until the intertetrahedral X...X distances are equal to the intratetrahedral distances (at this point the tetrahedra are beginning to “collide”) the T-X-T angle has been reduced to 129.6°, that is, close to the preferred Ge-O-Ge angle ($\approx 130^\circ$). Notice that the motion of the twelve inner X atoms corresponds exactly to the well-known^[30] transformation of a cuboctahedron to an icosahedron. Notice also that the eight outer X' atoms remain at the vertices of a cube.

We now look at simple ways in which T_8 cubes can be linked together to form three-dimensional frameworks. We are particularly interested in structures that can be constructed from regular TX_4 tetrahedra and in which all T-X-T angles are equal, and thus (as explained above) in the range $148.4^\circ \geq T-X-T \geq 129.6^\circ$. If two cubic units are linked by sharing an edge (i.e., two outer X' atoms common to both cubes) the angle involving these outer X atoms is $T-X'-T = 109.5^\circ$ (much too low for silicates or germanates), so we consider only configurations in which cubes are either linked by sharing corners or through intermediate atoms.

Figure 2 shows two simple ways of linking T_8 groups by corners. The first structure is known as polycubane (zeolite code ACO; Figure 2a) and the second as Linde A (LTA; Figure 2b). As shown in the figure, it is convenient to replace the $T_8X_{12}X'_8$ unit by a cube, so that one has structures of cubes

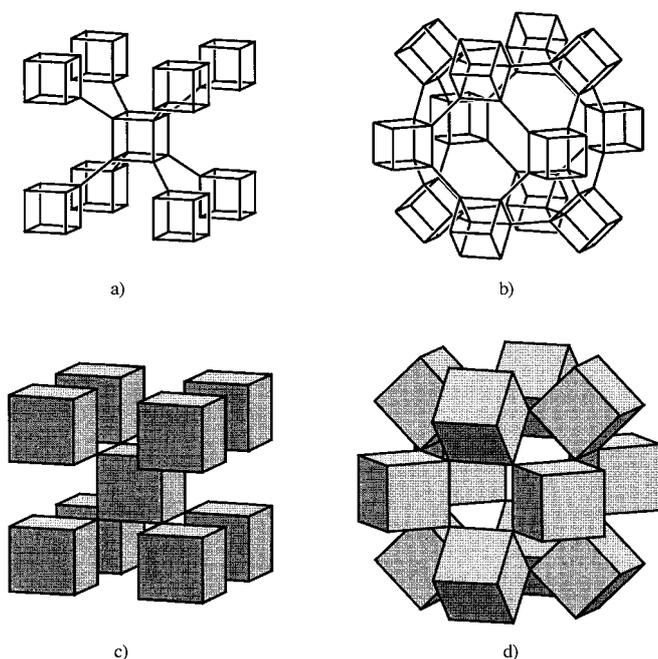


Figure 2. a) The T skeleton of the polycubane (ACO) net. b) The T skeleton of the Linde A (LTA) net. c) The ACO structure shown as corner-connected cubes which enclose T_8X_{20} units. d) A similar representation of the LTA structure as corner-connected cubes.

linked by corners. The $T-X'-T$ angle is the same as the angle formed by three points: a cube center, the linking X' atom, and the center of the adjoined cube. In the cubic conformations shown, the ACO structure has a $T-X'-T$ angle of 180° and the LTA structure has a $T-X'-T$ angle of 160.5° . It transpires that in ACO the $T-X'-T$ angle can be varied over a wide range by concerted rotations of the cubes about parallel fourfold axes, as described below, and this topology can be realized for all equal angles in the range $129.6^\circ - 148.4^\circ$. However, in the LTA framework the fourfold axes of the cubes (actually only twofold axes in the structure) are not parallel and the framework is rigid for regular cubes. Actually if the requirement of all equal T-X-T angles is relaxed, we find that the structure can be realized with regular tetrahedra and T-X-T angles in the range $145^\circ - 154^\circ$; this is suitable for aluminosilicates, but not favorable for germanates.

Figure 3 shows several conformations of the ACO topology. With T-X-T angles of 148.4° (Figure 3b) the symmetry is $P4/mnc$ and $c/a = 1.061$ (the cubic conformation has $c/a = 1.0$). To reduce the T-X-T angles the symmetry has to be lowered further. Each T_8 unit will have its fourfold axis reduced to a

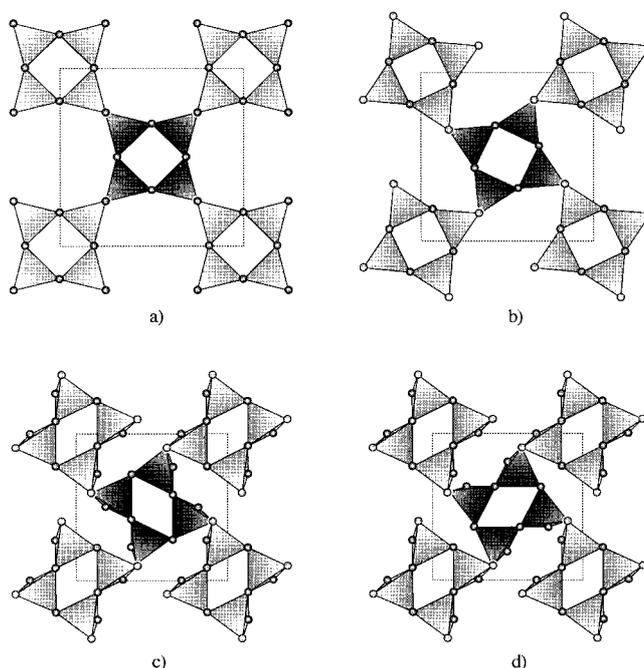


Figure 3. a) The cubic polycubane (ACO) structure with regular polyhedra projected on (001). b) The ACO structure with all T-X-T angles equal to 148.4° projected on (001) of the $P4/mnc$ cell. c) The ACO structure with all T-X-T angles equal to 129.6° projected on (001) of a $Pnmm$ cell. d) The structure obtained when the central TX unit in c) is rotated by 90° about an axis normal to the page. The symmetry is now $Cccm$ and the projection is on (001). (The cell outlined is a primitive cell). Notice that the darker shaded T_8 unit in the center of the unit cell has elevation differing by $c/2$ from those at the cell corners.

twofold axis, so there are two ways of orienting each of the T_8 units. The two simplest structures, shown in Figures 3c and 3d, have symmetries $Pnmm$ and $Cccm$, respectively, and $c/a = 1.021$ for $T-X-T = 129.6^\circ$. Clearly other ordered and disordered variations are possible. Actually, none of these structures has yet been found. The type of (and to date only) material^[32] for ACO has a framework of approximate composition $CoPO_4$: the symmetry is $I4m2$ with $c/a = 0.94$, the T-X-T angles range from $130^\circ - 169^\circ$, and in addition the CoO_4 tetrahedra are very irregular with O-Co-O angles varying from 82° to 124° , indeed Co has a fifth near-neighbor O atom. It would be nice to have an example of this elusive structure with more-nearly regular tetrahedra; certainly there is no geometric reason why it has not yet been found—with the possible range of T-X-T angles it is equally suitable for both silicates and germanates.

Figure 4 shows two simple ways of linking T_8 units by intermediate T atoms. The first structure, known as octadecasil (AST; Figure 4a), has $T-X'-T$ angles of 180° in its cubic form, but these can be reduced as for ACO, and again all T-X-T angles can vary in the range $129.6^\circ - 148.4^\circ$. With the maximum angle, shown in Figure 5b, the symmetry is $I4/m$ and

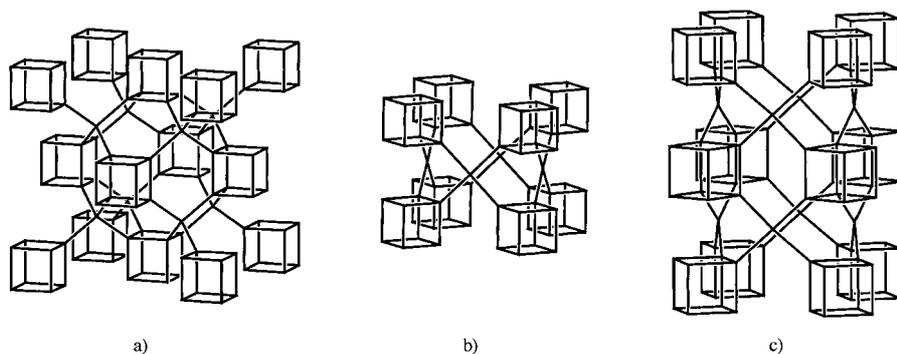


Figure 4. a) The T skeleton of the octadecasil (AST) net in its cubic ($Fm\bar{3}m$) conformation. b) The T skeleton of the ASU-7 net in its most symmetrical ($P4/mmm$) form. c) A structure with the topology of b) with a doubled cell and symmetry $P4/mmc$.

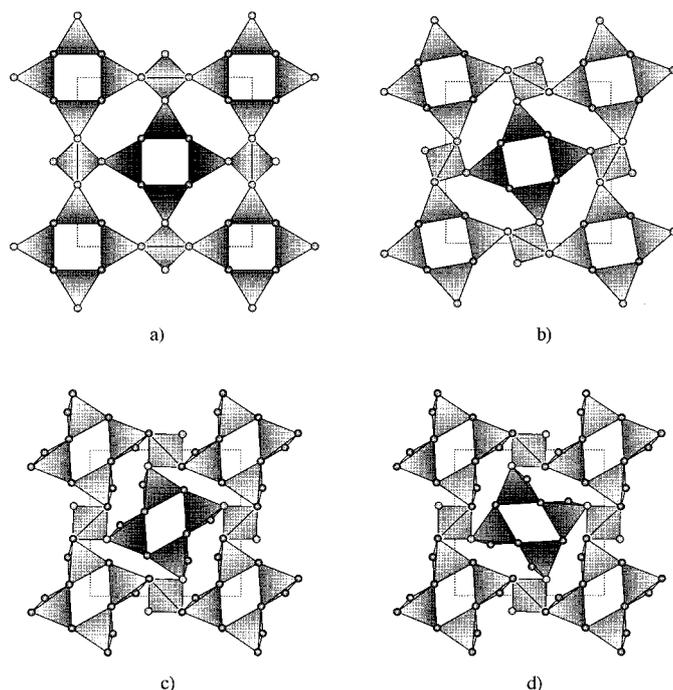
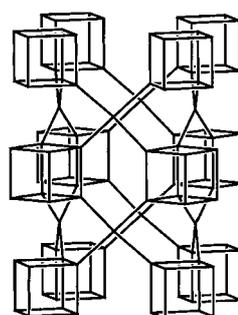


Figure 5. a) A projection of the ideal (cubic) octadecasil (AST) structure on (001). b) The AST structure with $T-X-T = 148.4^\circ$ and symmetry $I4/m$. The projection is on (001). c) and d) show two AST structures [with symmetries $I2/m$ and $P2/m$ respectively and projected on (010)] with $T-X-T = 129.6^\circ$. Note that the central T_8 unit is at an elevation differing by $c/2$ or $b/2$ from the elevations of those at unit cell corners (compare Figure 3).

$c/a = 1.48$. Real octadecasil^[33] with framework stoichiometry SiO_2 , is close to this conformation with $c/a = 1.46$ and Si-O-Si angles of $141^\circ - 149^\circ$.

Reducing the T-X-T angles in AST from 148.4° again destroys the fourfold symmetry and the two simplest structures with symmetries $I2/m$ and $P2/m$ are shown in Figures 5c and 5d. For T-X-T angles of 129.6° , $b/a = b/c = 1.60$. ASU-9^[4] has average symmetry $I4/m$ with $c/a = 1.53$, and the inner O atoms of the Ge_8O_{20} cubes are disordered over two sets of positions corresponding to the two possible orientations of each cube. The Ge-O-Ge angles range from $130^\circ - 133^\circ$. There are two isolated T atoms and one T_8 unit in the repeat unit of the structure, and ASU-9 is formulated as $Ge_{10}O_{20} \cdot DABCO \cdot H_2O$ (DABCO is 1,4-diazabicyclo[2,2,2]-octane).



Clearly then the AST structure, like that of ACO, is equally suitable for silicates and germanates, although in the latter orientational disorder is expected to be the norm. It might be mentioned that in unpublished work we have also found the AST topology in a material with framework composition $GaGe_4O_{10}$. It has very similar structural parameters to ASU-9 including oxygen disorder over two sets of positions.

Finally, we turn to the structure in Figure 4b. In its simplest conformation, which has symmetry $P4/mmm$, T atoms linking the T_8 units are at centers of symmetry, and hence are unsuitable to be the site of a tetrahedrally coordinated atom. Such a structure might be rejected by a structure designer (and to our knowledge, was not earlier predicted), but simple rotation of cubes, now in alternating senses along parallel fourfold axes, makes the site suitable to serve as the center of a regular tetrahedron. If the structure is constructed with T_8 units with fourfold symmetry, the symmetry is $P4/mcc$, the T-X-T angles are 148.4° , and the T-X'-T angles are 131.5° ; so, as it stands, it is not ideally suited either for silicates or for germanates. However, as before, the T-X-T angles in the T_8 units may be decreased and, in fact, all T-X-T angles can be made equal at the special value of 131.1° ; this happens to be an angle ideal for germanates. The simplest structure has symmetry $Pccm$ and $c/a = c/b = 1.59$ as shown in Figure 6b. ASU-7 has this structure, with average symmetry $P4/mcc$ and $c/a = 1.65$ (Figure 6a). The O atoms are disordered over two sets of positions (corresponding to the two possible orientations of the Ge_8 units, and Ge-O-Ge angles are in the range $126^\circ - 132^\circ$. The number of tetrahedra in the repeat unit is the same as for AST, and ASU-7 is formulated as $Ge_{10}O_{20} \cdot DMA \cdot H_2O$ (DMA = dimethylamine). Notice that in ASU-7 there are one-dimensional channels in contrast to the closed cages in AST (compare Figures 4 and 6). The material in the channels can readily be removed (e.g., by calcination) and pure GeO_2 with the same open structure retained (the density is almost exactly one half that of the rutile form of GeO_2).

It is of interest that ASU-7, ASU-9,^[4] and octadecasil^[33] were made from a fluid phase containing fluorine, and in all cases electron density corresponding to H_2O or HF was found at the centers of the cubes. In the case of octadecasil, NMR spectroscopy provided convincing evidence for an F atom located at the center of the Si_8 cube,^[34] and this may be an important ingredient in the successful synthesis of other frameworks containing T_8 units.

Our analysis has shown that the observed O disorder in ASU-7 and ASU-9 is to be explained as the occurrence, presumably essentially at random, of Ge_8O_{20} units in one of two possible orientations that are frozen statically in place. Such a situation has been termed an "orientational glass".^[35]

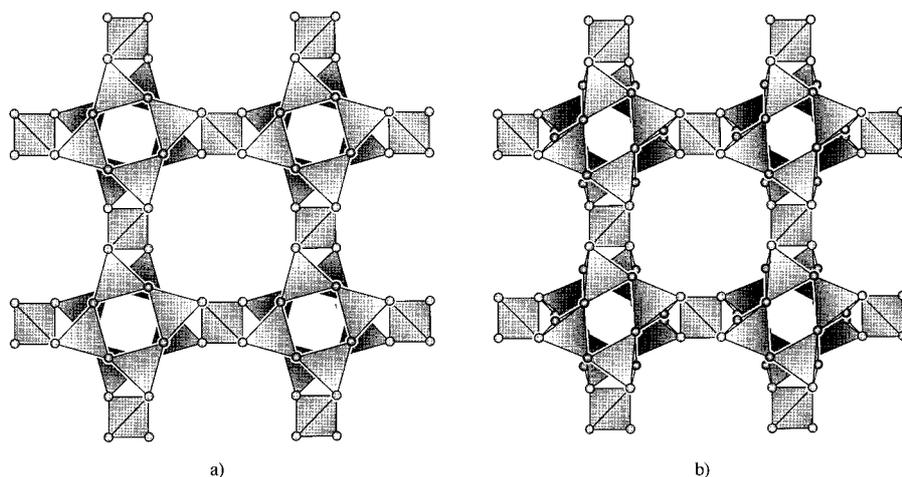


Figure 6. a) The framework of the ASU-7 structure with T-X-T angles of 148.4° in the T_8 units. Projection on (001) of the $P4/mmc$ cell. b) The same topology but with all T-X-T angles equal to 131.1° . The symmetry is $Pccm$ and the projection is on (001).

Conclusion

The analysis of structures containing T_8 units has shown that some structures, specifically those of ACO and AST, can be realized with regular tetrahedra and with a range of T-X-T angles including those suitable for both Ge-O-Ge and Si-O-Si configurations. On the other hand the structure of ASU-7 can only be made with regular tetrahedra if the T-X-T angle is 131.1° and thus it is suitable for Ge-O-Ge, but not for Si-O-Si. The LTA structure cannot be made at all with regular tetrahedra and all equal T-X-T angles, but can be made with a small range ($T-X-T = 145.3^\circ - 154.5^\circ$) that is close to ideal for Si-O-Si, but not suitable for Ge-O-Ge.

Thus, in the study of germanates and related materials, it might be expected that some common silicate structures either do not occur or are difficult to synthesize. The other side of the coin is that we might expect to find some novel zeolitelike nets in germanates. We have adduced the structure of ASU-7 as an example of the latter. Another example is found in the beautiful tetrahedral framework structure of UCSB-7,^[20] which has composition of, inter alia, $GaGeO_4$. We have determined that this structure can only be made with regular tetrahedra and equal T-X-T angles if $T-X-T = 129.8^\circ$. It is unlikely therefore to be found in an aluminosilicate or aluminophosphate.

A recent development^[36] has been the construction of very open frameworks built up of "supertetrahedral" units of sulfide tetrahedra. These require T-S-T angles close to 109° , so they may not be expected to form many zeolite nets. We remark, however, that the cristobalite and sodalite nets can be made with regular tetrahedra over a wide range of T-X-T angles and these two topologies are found in a wide variety of materials including the new sulfides.

We propose to undertake a comprehensive study of configurations of corner-lined tetrahedra from the point of view of this paper. The development of germanate frameworks with mixed coordination (tetrahedra, octahedra, etc.) suggest that eventually the analysis should be extended to these cases also.

Acknowledgment

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