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Where zeolites and oxides merge: semi-condensed tetrahedral frameworks

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The synthesis of new inorganic materials constructed with extended lattices has taken place mainly in two areas, complex oxides and porous framework structures. In the former case the drive has been towards controlling electronic and magnetic properties while in the latter domain porosity and the ability to enclathrate small organic or inorganic units has been paramount. Semi-condensed framework materials, whose compositions and structures place them at the borderline of these two classes, are described in this article, such compound types include the sodalite, cancrinite, analcime, zeloites ABW and JBW and scapolite structures. In each case recent chemistry and developments are described particularly with respect to advances made at The University of Southampton. The potential for merging the properties and structures of these two classes of compounds are also discussed.

Mark Weller currently occupies the Chair of Materials Chemistry at the University of Southampton. He was born in 1960 and after completing degrees at Oxford University took up a lectureship in the Department of Chemistry in Southampton in 1985. His research interests are in synthetic and structural solid state chemistry and materials studied range from complex oxides and nitrides, including phases related to the cuprate superconductors, to framework structures, such as zeolites. The applications of such materials as pigments, ion exchangers and in optoelectronic devices are also studied. Novel structure determination methods involving neutron diffraction and EXAFS are also being developed in his group. He was awarded the RSC Meldola Medal in 1990.

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Introduction

Two of the major topics in the area of inorganic solid state chemistry that underwent rapid development at the end of the 20th century were those concerned with zeolites and with complex metal oxides. In the former category open framework materials for catalysis, ion exchange and adsorption have been developed while in the latter topics such as high temperature superconductivity, colossal magnetoresistance and fast ion conductors/fuel cells have been major areas for the development of novel structure types and the synthesis of new inorganic compounds. A common feature relating these areas is that both families of compounds are based on oxygen, either in linked AO_4 tetrahedra, where A is normally a post transition element, as with zeolites, or with a variety of MO_n polyhedra such as octahedra, square based pyramids and square planes in complex oxides. This article concerns inorganic chemistry at the borderline of the two classes of compounds where a number of structure types based on linked oxotetrahedra exist that promise to fuse the properties of these key inorganic materials.

Zeolite structures can be defined as fully cross-linked framework materials built from *tetrahedral* units in which the framework density, the number of tetrahedral atoms (T atoms) per 1000 Å^3, is lower than about 20–21. These low framework densities are the result of the pores and cavities, which often contain extra-framework cations, water or absorbed molecules, though in some structures with neutral frameworks the channels can effectively be empty. At higher framework densities are the tectosilicates, where each TO_4 unit is linked through oxygen to another, such as the silicon dioxide polymorphs quartz, cristabolite and tridymite and minerals such as albite and scapolite, Fig. 1. Using the normal classification basis over 100 zeolite and zeolite-like structures have been described.[1]

Strictly speaking, the term zeolite should be applied only to aluminosilicates but the family of zeolite-like materials constructed from TO_4 units now extends to T atoms such as P, Ga, Ge, B, As, Be.... with aluminophosphate and silicoaluminophosphate structures now comprising a significant proportion, about 45, of the catalogued "zeolite structures". Structures where gallium and germanium replace aluminium and silicon respectively in the zeolite framework are also reasonably common, for example the materials Ge-RHO[2] and gallogermanate-LTA[3] represent the ease with which these species can adopt tetrahedral co-ordinations. Even so the tetrahedral framework

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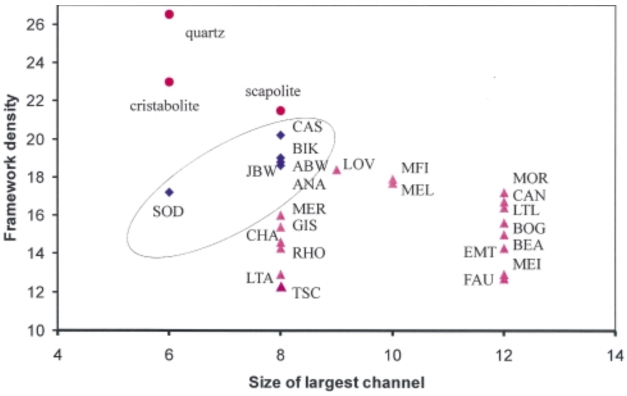

Fig. 1 Framework density *versus* maximum ring opening size for a range of tetrahedral frameworks. Frameworks are divided into three regions corresponding to dense oxide-like structures (●), open porous zeolites (▲) and intermediate structure types (◆).

chemistry of such species is probably limited by an inclination towards higher co-ordination numbers, due to their greater ionic size. For example, in complex oxides such as gallium tantalate $GaTaO_4$[4] and the series of ULM gallium phosphates[5] octahedral and five-co-ordinate gallium centres exist. Other elements that adopt tetraoxoanionic species in their compounds are Co, Ti, Fe, Mg and Ni but with decreasing occurrence. In terms of zeolite structures cobalt is found at appreciable levels in materials such as ABW,[6] SOD,[7] and LAU[8] reflecting the stability of the d^7 species due to crystal field stabilisation energy considerations in the tetrahedral co-ordination. Ions such as Fe^{2+} and Ni^{2+} rarely adopt tetrahedral co-ordination in complex oxides or framework structures[9] though they do so reasonably often in their compounds with other ligands. In classical complex oxides, ions such as Fe^{2+} and Ni^{2+} are normally found in sixfold co-ordination.

As well as framework density and the nature of the T atoms other criteria can be applied to the definition of a true zeolite material, such as the existence of voids connected through various sized rings and the presence of water within the structure. The size of the rings forming the connecting pores ranges from 6 to 20 in materials such as cloverite but nearly all true zeolites exhibit one pore opening constructed from at least eight tetrahedral units, unlike non-zeolitic materials such as quartz (maximum ring size 6); an exception is hydrosodalite $Na_6[AlSiO_4]_6{\cdot}8H_2O$ with a maximum aperture of a 6-ring.

Other inorganic oxide structures can be considered as framework materials but would probably be classed as complex oxides rather than zeolite-like materials. In terms of complex oxide structures the metal co-ordination in the polyhedra forming the structure is generally higher than four and based typically, for a first row transition element, around octahedra. This includes the perovskite based structures of high temperature cuprate superconductors and complex manganese oxides displaying colossal magnetoresistance, which are most easily considered as derived from linked CuO_6 and MnO_6 octahedra, though these are often very oxygen deficient in the former case, reducing the copper co-ordination number to four (square planar rather than tetrahedral) or five. Other complex oxide structures such as $CrPO_4$ and $NbO(PO_4)$ contain octahedral metal co-ordination in association with tetrahedral phosphate and silicate. However, lower co-ordination geometries can occur reasonably frequently in so called complex oxide structures. For example, metal phosphates, such as $KNiPO_4$,[9] and garnets, *e.g.* $Mg_3Fe_2(SiO_4)_3$, would be classed as complex oxide structures but contain NiO_5 square based pyramids and FeO_4 tetrahedra respectively. In addition to oxides, compounds such as metal hydrogenphosphates,[10] carboxylates[11] and borophosphates[12] generally have metal co-ordinations higher than tetrahedral, particularly when the material is obtained from solution. The range of such "framework materials" has undergone a rapid expansion in the last few years particularly with the application of hydrothermal synthesis methods, applied mainly to zeolites previously, to non-aluminosilicate systems. Families of such materials include the titanosilicates,[13] molybdenum and uranium phosphates[14,15] and nickel phosphates;[9] the synthesis of many of these new materials has been reviewed recently.[16]

Obviously the definition of what is and what is not a zeolitic or zeolite-like material is becoming increasingly vague both in terms of the composition of the framework, the type of polyhedral units forming the framework, levels of hydration and pore structure/framework density. This article concerns a group of materials which all have structure types that allow them to be classed formally as among the zeolites, with structures formed from linked tetrahedra, but their chemistry is such that many of their characteristics and physical properties are closer to those of complex oxides. The versatile nature of the zeolite framework, in terms of structural and compositional flexibility, coupled with the presence of the zeolite-defining channels and pores, which may be occupied by a range of simple inorganic species, produces an exceptional and fascinating range of materials. Coupling this structural and compositional flexibility of zeolites to that of oxides, through the incorporation of structural and compositional fragments which are normally associated with, for example transition metals or ionic salts, produces several families of hybrid inorganic compounds. The properties of these materials are such that they are related to those of zeolites, for example in being able to display ion exchange behaviour and the trapping of nanounits of simple inorganic species within the cavities, and to those of complex oxides with high levels of transition and post transition metals which have applications related to, for example, magnetic, optical and electronic effects. As such the area is proving rich for the development of new inorganic materials with application oriented properties.

The semi-condensed zeolites

Zeolite structure types that lie on the borderline of being considered as complex metal oxides may be selected from the 126 synthesized topologies through a number of criteria. Obviously framework density can be used to distinguish such phases and only denser structures approaching the upper limit of 20 or 21 tetrahedral atoms per 1000 Å^3 can be considered. However on this basis hydrosodalite $Na_6[AlSiO_4]_6.8H_2O$ with a framework density of 16.7 is typical in comparison with zeolites in general, though it should be noted that, depending upon composition, sodalites can have framework densities between 15.5 and 22.[17] Other criteria which can be applied to distinguishing a semi-condensed framework are whether the framework topology can be synthesized directly for certain compositions without adsorbed water, which is related to some extent to the size of the pores in the material, and the value of the framework charge, which in aluminosilicates is, of course, dictated by the silicon : aluminium ratio. Zeolite structures which can be synthesized with an aluminium to silicon ratio of 1 : 1 are relatively rare. The few examples include zeolite A (LTA),[18] sodalite (SOD),[19] cancrinite (CAN),[20] zeolite P (GIS)[21] and zeolite X (FAU),[22] though the last two materials are difficult to prepare with high aluminium contents requiring careful control of the synthesis conditions. One problem with zeolite structures containing high levels of aluminium is the reduced hydrothermal stability of open hydrated frameworks probably as a result of the weak Al–O–Si linkage compared with Si–O–Si. In the denser frameworks *e.g.* SOD non-hydrated, non-framework cations can help stabilise the Si–O–Al bridge by strong co-ordination to the otherwise under-bonded oxygen atom. Hence, high aluminium content aluminosilicates are generally found only for structures with small pore sizes, mainly 6 and 8 rings though maximum aluminium faujasite (zeolite X) with 12 rings is an exception.

A further criterion that can be applied when considering materials that lie on the borderline between zeolites and complex oxides is whether the zeolite type framework can be synthesized without solvent molecules co-ordinating to cations that are present in the pores. Anhydrous structures built from aluminophosphate or pure silica building units with no or few extra framework cations are excluded from this. Consideration of the classified zeolite structure types[1] shows that of these the structure codes CAS, ANA, BIK, SOD and ABW fit this description, as does the JBW structure in part (only a portion of the cations are hydrated). It is noteworthy that the framework density of these materials is generally towards the upper limit of the range characterised by zeolites and the ring sizes are restricted to 8 members or less, Fig. 1. It is these materials which are the main subject of this paper. The feldsparthoid family of compounds such as nepheline (Na,K)$AlSiO_4$ and petalite, $LiAlSi_4O_{10}$ which are defined as *anhydrous* framework aluminosilicates that contain alkali/alkaline earth metals do not have *any* member that can contain water,[23] which distinguishes them from the majority of materials in this article. In addition to these semi-condensed zeolite structures three other structure types are also described, cancrinite, tschoertenerite and scapolite structures, which while displaying either the full characteristics of a zeolite (cancrinite and tschoertenerite) or the lack of an interconnected pore structure and hydrated member (scapolite, a feldsparthoid) all unusually contain anions trapped within the structures and are of interest in relation to the incorporation of simple inorganic species within frameworks.

Members of each of these classes, sodalite (SOD), cancrinite (CAN), analcime (ANA), ABW, JBW, CAS (caesium aluminium silicate), TSH, bikiatite (BIK) and scapolites are considered in turn. As well as describing the new inorganic chemistry that has recently been achieved with each of these material types, emphasising the authors research, the different materials are considered in terms of their unusual structures that can lead to specific application based properties.

Sodalites

The most widely studied materials in this class of semi-condensed zeolites are those belonging to the sodalite family. Many sodalites can be described by the general formula $M_8[ABO_4]_6X_2$, where M is a monovalent cation such as Na^+, Li^+ and Ag^+,[24,25] A and B are tetrahedral forming species such as Al and Si, and X can be a variety of mono- or di-valent anions, including Cl, Br, I,[26,27] ClO_3^-,[28] MnO_4^{2-} [29] and CrO_4^{2-}.[30] The structure is based upon a truncated octahedral cage linked in three dimensions,[24] yielding four- and six-membered rings which are directly linked to form the overall structure, Fig. 2. Compositional variations are numerous within this basic structure type and include additional trapped anions such as in bicchulite $Ca_8[Si_4Al_8O_{24}](OH)_8$ [31] and $Nd_4[Al_{12}O_{24}](Pb_4O_4)_2$ [32] or no trapped anion as in $Na_6[AlSiO_4]_6 \cdot nH_2O$ [33] and the sodalite electrides *e.g.* $Na_8[AlSiO_4]_6$.[34]

The aluminosilicates are by far the most well known and characterised sodalites, in which a monovalent anion typically resides at every cage centre and is co-ordinated to sodium ions resulting in the formation of M_4X clusters in each beta cage.[26] Sodalites are generally synthesized with Na^+ as the non-framework cation, which can then be exchanged in aqueous solution by a range of other monovalents such as Li^+, K^+, Rb^+ and Ag^+;[25] such behaviour is clearly that of a porous zeolitic structure. The general formula of the aluminosilicate sodalites (and those with isomorphous substitutions for example Ga for Al and Ge for Si) can therefore be rewritten in the terms $[\mathrm{FRAMEWORK}]^{6-}[M_8X_2]^{6+}$ allowing these materials to be described as a solution of simple inorganic ionic material [M,X] with the framework acting as the solvent, Fig. 3.

Several sodalite sub-groups exist including noselites,[35] hauynes[36] and perhaps the most important of all sodalite species, the ultramarines,[37–39] see below. Noselites have divalent anions only in alternate β cages, while in the hauyne sub-group two sodium cations are replaced by divalents, with the extra positive charge compensated by the existence in each cage of divalent oxoanions. The general formula for a hauyne is thus written $M^{2+}{}_2M^+{}_6[ABO_4]_6(XO_4)_2$, where M includes Ca,[35] Sr, Cd, Mn and Pb[40] and X includes S, Mo, W and Cr.[41] The filling of only alternate cages obviously produces a different array of trapped inorganic species yielding a new set of interactions between the centres, Fig. 3. The structures of the chromate and tungstate hauynes have been investigated in detail due to the orientation ordering of the non-framework tetraoxoanion and the endowment of pyroelastic properties.[42]

A variety of framework substitutions has also been reported indicating the stability of the basic sodalite cage, Table 1; as well as simple cation replacements, the sodalite cage may be formed from other anionic species such as nitride and chloride. The most common trivalent species incorporated into the framework is gallium, which can totally replace aluminium; similarly germanium can supplant silicon, and together these give rise to frameworks of formulae $(GaSiO_4)_6{}^{6-}$,[43] $(AlGeO_4)_6{}^{6-}$ [44] and $(GaGeO_4)_6{}^{6-}$,[45] with properties similar to their aluminosilicate analogues. Examples of some of the phases we have recently synthesized[46] include $Na_8[AlGeO_4]_6(X)_2$, with $X = ClO_4^-$, ClO_3^-, SCN^-, NO_2^-, HCO_2^- or MnO_4^-, $Na_8[GaSiO_4]_6(X)_2$ with $X = SCN^-$, NO_2^- or HCO_2^- and $Na_8[GaGeO_4]_6(X)_2$ with ClO_4^-. The structure of $Na_8[AlGeO_4]_6(HCO_2)_2$ determined using powder neutron diffraction is shown in Fig. 4 and pin-

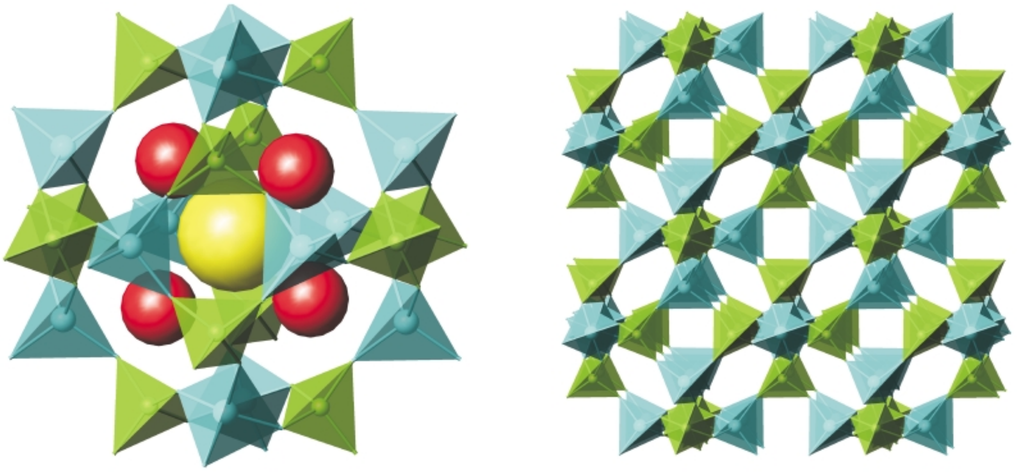

Fig. 2 The sodalite structure, $Na_8[AlSiO_4]_6Cl_2$. The linking of alternate SiO_4 (green) and AlO_4 (blue) tetrahedra forms a body centred arrangement of framework β cages, right. Each cage contains a central anion (yellow) surrounded tetrahedrally by cations (red), left; the cations also interact strongly with three framework oxygen atoms to produce a distorted tetrahedral environment for these ions.

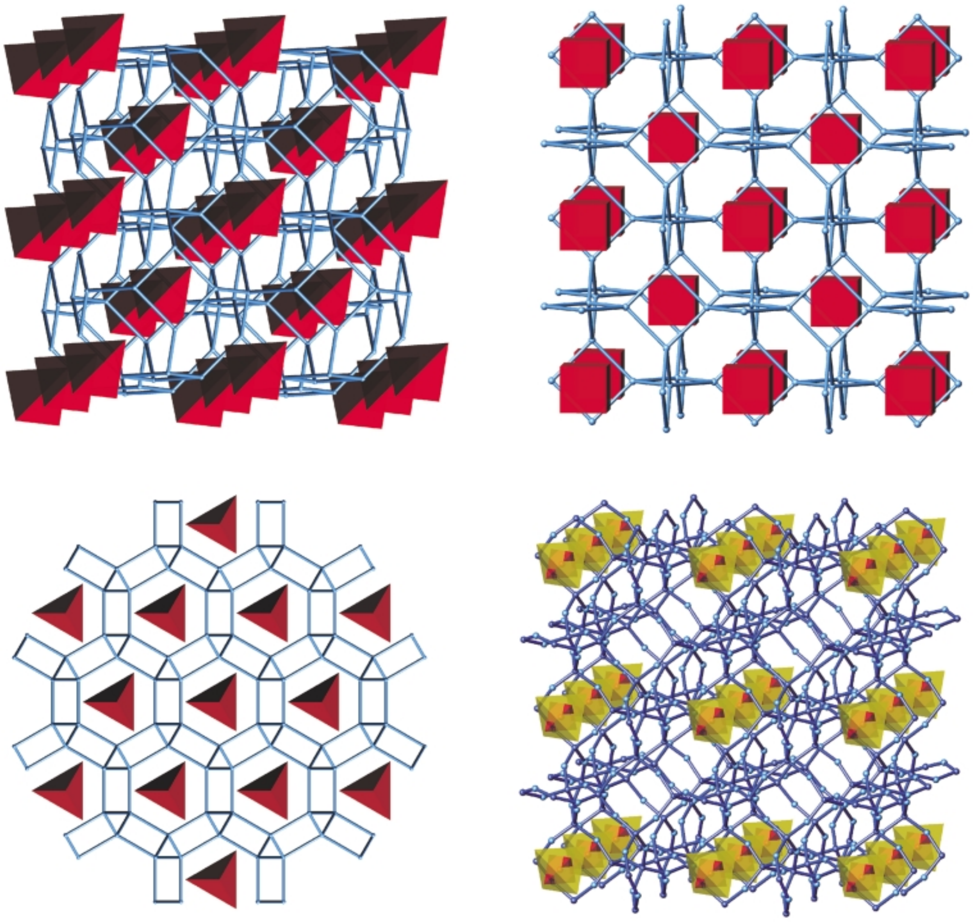

Fig. 3 Arrays of inorganic blocks in sodalite derived structures. Anti-clockwise from top left: face centred array of M_4X tetrahedral units as in $M_8[BeSiO_4]_6X_2$ viewed close to [100], face centred cubic array of M_4X tetrahedral units as in $M_8[BeSiO_4]_6X_2$ viewed down [111], body centred array of interpenetrating double $M_4(AO_4)$ tetrahedral units as in noselites $M_8[AlSiO_4]_6AO_4$ and face centred array of M_4X_4 cubes as in bicculite $M_8[AlO_2]_{12}X_8$.

Table 1 Framework compositions of sodalite type structures

Framework atoms	Example
Si,Al	$Na_8[SiAlO_4]_6Cl_2$
Si	$[SiO_2]_{12}(C_2H_4(OH)_2)_2$
Si,Ga	$Na_8[SiGaO_4]_6(HCO_2)_2$
Ge,Al	$Na_8[GeAlO_4]_6(MnO_4)_2$
Ga,Al,Si	$Ca_8[GaAlSiO_6]_4(OH)_8$
Ge,Ga	$Na_8[GeGaO_4]_6(ClO_4)_2$
Al,Be,Si	$Na_8[AlBeSi_4O_{12}]_2Cl_2$
BeSi	$Cd_8[BeSiO_4]_6Se_2$
Al	$Ca_8[AlO_2]_{12}Te_2$
B	$Ca_8[BO_2]_{12}S_2$
AlP	$[AlPO_4]$
Mg	$Na_8[Mg_3Si_9O_{24}](OH)_2$
ZnP/ZnAs	$Na_6[ZnAsO_4]_6{\cdot}8H_2O$
P	$H_4Co_5[P_{12}N_{24}]Cl_2$
Zn/Cu	$[HN(CH_3)_3][Zn_5CuCl_{12}]$
Co/P	$[NMe_4][CoPO_4]$

points the position of the formate ion with respect to the extra-framework cations and the framework itself. The position of these anions and other small organic species have been determined within the sodalite cage and such information is useful in understanding the interaction of these species with tetrahedral frameworks and in relation to absorption and catalysis.

It is noteworthy that the gallogermanate sodalite family is far less extensive than that containing the smaller tetrahedral species SiO_4 and AlO_4 once again demonstrating the relative difficulty in forming frameworks based on tetrahedral gallium and germanium. As with the aluminosilicate sodalites, post phase formation reactions may be undertaken on these framework substituted sodalites including ion exchange and partial thermal decomposition of the entrapped species. In this way materials such as $Li_8[GaSiO_4]_6(NO_2)_2$ can be produced,[46] through ion exchange with aqueous Li^+, as can analogues of ultramarine, see below. Thus heating $Na_8[AlGeO_4]_6(SCN)_2$ in air results in the intra cage decomposition and oxidation of the thiocyanate group yields S_2^- and S_3^-, producing the blue-green $Na_8[AlGeO_4]_6(S_2, S_3)_x$.[47]

Incorporation of divalent species such as Be^{2+}, Mg^{2+} or Zn^{2+} [45] instead of Al^{3+} leads to an increased negative charge on the framework which is normally compensated for by the inclusion of divalent non-framework cations such as Ca^{2+}, giving rise to stoichiometries such as $Ca_8[BeSiO_4]_6(SO_4)_2$.[48] Similar stoichiometries arise from frameworks in which there is only one framework tetrahedral species as a trivalent, for example $Ca_8[AlO_2]_{12}S_2$.[49] Bicchulite, $Ca_8[Si_4Al_8O_{24}](OH)_8$,[31] and a gallium substituted analogue $Ca_8[Si_4Ga_4Al_4O_{24}](OH)_8$ [50] are similarly unusual members of the zeolite family in that the frameworks contain a trivalent to tetravalent ratio of greater than unity producing a very negatively charged framework $[TO_2]^{1.5-}$. The formation of the Al–O–Al links in bicchulite is presumably a result of its synthesis under moderate temperature, high pressure and non-aqueous solution conditions. The presence of four calcium ions and four hydroxide groups in each β cage represents the highest level of filling that has been achieved for this cage size with 12 atoms and the structure is stabilised by moderately strong hydrogen bonds to the framework oxygen atoms. The structure of bicchulite, which is formed from the disordered arrangement of locally ordered domains, has been studied in detail using a combination of neutron diffraction and Ga-edge EXAFS.[51] Gallobicchulite, $Ca_8[Si_4Ga_4Al_4O_{24}](OH)_8$, is the only known example of a tetra-

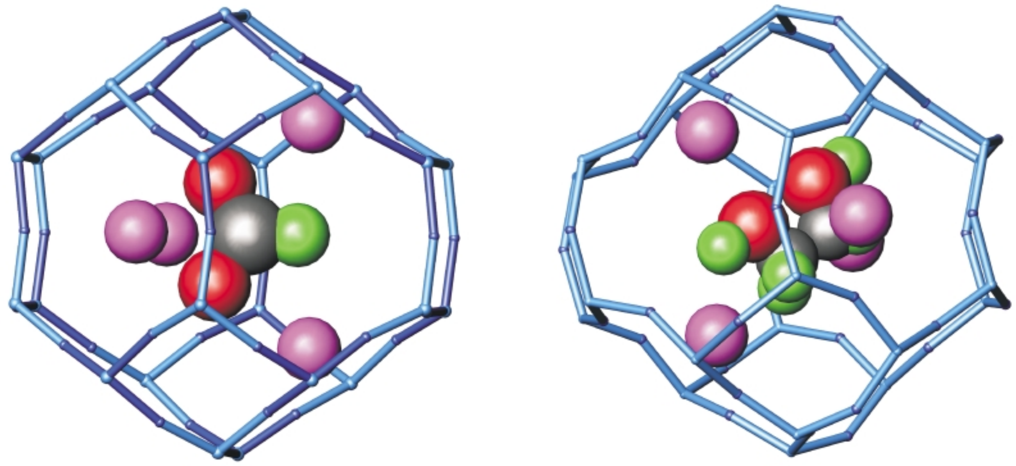

Fig. 4 The sodalite cage of formate aluminogermanate sodalite $Na_8[AlGeO_4]_6(HCO_2)_2$ showing the position of the formate ion as determined from powder neutron diffraction (left); the sodium ions are also shown (magenta). The sodalite cage of ethylene glycol silica sodalite showing the position of the organic species is given at the right; the sodium ions are also shown (magenta). Key: carbon, grey; oxygen, red and hydrogen, green.

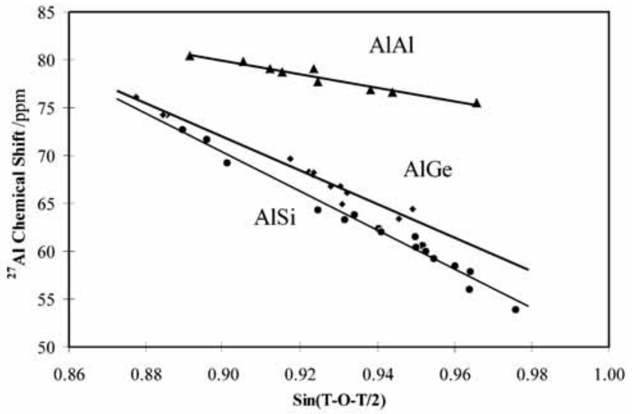

Fig. 5 Typical structure–MAS NMR chemical shift relationship derived from sodalite structures with variations in the ^{27}Al chemical shift position plotted as a function of sin [(Al–O–T)/2]. (T = Al, Ge or Si). This sine function has widely been used in the literature to describe effect of the T–T separation on chemical shift.

hedral framework material with an oxygen bridge between two tetrahedral gallium sites.[50]

Owing to the extreme compositional and structural flexibility of the framework, the T–O–T bond angle varying over the range 120–150° as a function of β-cage content, the sodalite family forms an excellent model for relating various physical properties to structure. Such models and derived correlations can then be applied to the full range of zeolitic framework compounds where structure determination is often very difficult. Areas where this has been applied include thermal expansion, vibrational spectroscopy and, particularly, solid sate NMR.[52,53] Excellent correlations between framework structural parameters such as T–O–T bond angle or the distortion of the TO_4 units with chemical shift and other NMR determined parameters have been determined. Classically such correlations have been obtained for ^{29}Si MAS NMR data and functions of the framework Si–O–Al bond angle in aluminosilicate frameworks, but such correlations have been extended to ^{27}Al, ^{71}Ga and ^{9}Be with a variety of different T–O–T′ links by work in Southampton,[53] Fig. 5. Through the use of such model data it is possible to obtain information, such as the local T–O–T bond angles, on the environment of tetrahedral species doped into other zeolite or tetrahedral frameworks.

Hydro- and hydroxy-sodalites. Enclathrated organics. The true zeolitic sodalites

The true zeolitic sodalites belong to the family $Na_6[AlSiO_4]_6 \cdot nH_2O$, $n = 0$, 4 or 8.[33] With no anion present in the cage there is room for water molecules and the series of compounds $n = 0$–8 may be synthesized by reaction of kaolin and sodium hydroxide under hydrothermal conditions to yield hydroxysodalites from which hydroxide ions are removed by Soxhlet extraction. In $Na_6[AlSiO_4]_6 \cdot nH_2O$ each β cage contains on average three cations and four water molecules positioned at the corners of a cube[54] in similar positions to those of the calcium and hydroxide ions in bicchulite. Hydroxy- and hydro-sodalites are of interest as they are formed along with cancrinites in the Bayer process of aluminium extraction.[55] Some small organic (solvent) molecules may be trapped in the sodalite cage when it is formed directly from non-aqueous solvents for example ethylene glycol,[56] Fig. 4, and 1,4-dioxane.[57]

Phosphonitride and copper chloride structures

The stability of the basic sodalite β cage can be seen from the formation of this structural feature in other, non-pure oxo, materials that are built from linked tetrahedra. For example the $P_{12}N_{24}$ unit replacing the $Al_{12}O_{24}$ unit, is found in phosphonitride chemistry in the compound $Zn_7[P_{12}N_{24}]Cl_2$.[58] Mixed oxonitrido frameworks yield greater compositional flexibility in the materials $M_{8-m}H_m[P_{12}N_{18}O_6]Cl_2$ (M = Cu or Li) with a sodalite-like $[P_{12}N_{18}O_6]^{6-}$ framework of corner-sharing PN_3O tetrahedra synthesized by the reaction of the respective metal chlorides with $(NH_2)_2PONP(NH_2)_3$.[59] No experimental evidence for a crystallographic ordering of the N/O atoms in the sodalite framework has been obtained.

The halozeotype CZX-1 also adopts the sodalite structure with a framework of stoichiometry $[CuZn_5Cl_{12}]^-$ containing orientationally disordered trimethylammonium ions. This material has a highly contracted framework with a T–Cl–T angle of only 110°, which can be achieved as a result of the long T–Cl bond of 2.285 Å.[60]

Electro-sodalites

Sodium electro-sodalite is prepared by absorbing one additional sodium atom in each cage of the anion free sodalite $Na_6[AlSiO_4]_6$.[34] The large electric fields inside the cages result in the formation of clusters of the type $[(Na^+)_4(e^-)]$ in which the alkali atom is ionised and the donated electron shared among several ions. The resulting material can be considered to behave as a body centred cubic sub-lattice of F-centres. Similar materials with other alkali metal ratios may be prepared *e.g.* $[Na_3K]$. At low temperatures the free electrons in these materials order antiferromagnetically (T_N 50–70 K), an unusual feature for s electrons.[61] However, these materials are not metallic indicating that electrons are trapped within the sodium cluster in the sodalite cage; such behaviour can be compared with that of the more open pore zeolites where high loading of metals leads to metallic behaviour.

Inorganic nano-units/semiconductors in sodalites

The presence of both cations and anions within the β cage is an unusual feature of the sodalite structure shared only by the cancrinite/afghanite/liottite series of materials and tshoertnerite among the recognised zeolite structures, though anions may be trapped in a few other silicates such as scapolite, see below. The presence of both cations and anions within the cage allows the sodalite structure to be viewed from a different perspective in that it can be considered as small units or nano-units of ionic inorganic compound dispersed in the framework, Fig. 3. In the case of most sodalites this unit is merely a $[M_4X]^{3+}$ [M = Na, Ag ….; X = Cl] or a $[A_4Y]^{6+}$ [A = Ca or Cd; Y = O, S ….] tetrahedral moiety that represents a chunk of a tetrahedral structure such as zinc blende. In materials such as bicchulite and $Ln_4[Al_{12}O_{24}](Pb_4O_4)_2$ the trapped portion is of stoichiometry M_4X_4 with a more widely dispersed rock salt arrangement of nano-units. These trapped nanoparticles are of course perfectly regularly arranged within the sodalite cages, Fig. 3. However there seems to be no electronic communication between the centres as observed in optoelectronic studies.[62]

Ultramarine and the stabilisation of reactive inorganic species

Ultramarine, $Na_{8-x}[AlSiO_4]_6(S_3,S_2,SO_4,Cl\ \ldots)$, has been used as a pigment since ancient times and is the compound responsible for the colour of the semi-precious mineral lapis lazuli. It is used extensively as a pigment in cosmetics and plastics and its chemistry and applications have recently been reviewed.[38]

There are several forms of ultramarine, containing sulfur in various polyanionic forms. The yellow, green, blue, pink, red and violet forms have all been reported as being caused by polysulfide radical species S_n^- entrapped in the sodalite cages.[39,63] Diffuse reflectance spectra for ultramarine yellow and blue show bands at approximately 400 and 600 nm respectively assigned to S_2^- ($^2\Pi_{1/2u} \longleftarrow {}^2\Pi_{3/2g}$) and S_3^- ($^2B_1 \longleftarrow {}^2A_1$).

The incorporation of the S_3^- ion provides an excellent example of the stabilising effect of the sodalite cage, since no simple salts of S_3^- exist due to rapid dimerisation upon addition of counter ions to its solutions. The structure of commercial ultramarine blue was first investigated in detail by Barnes and co-workers[63] who modelled the structure using neutron diffraction data. The relatively low level of cage filling by S_3^-, the low symmetry of this species in comparison with the sodalite cage resulting in positional disorder and the presence of impurities in commercial ultramarines, typically 15% of the material, results in difficulties in modelling the ultramarine structure. The best structural model consisted of formally bent S_3^- units, obtained by occupying three meridional vertices of an octahedron, located near the cage centres, but the large thermal parameters associated with this species indicate that this model is not perfect.

Recently, we have studied the structures of a pure laboratory synthesized ultramarine blue with a high sulfur, as S_3^-, content and also ultramarine yellow/green, in which the trapped species is mainly S_2^-, using a combination of powder X-ray diffraction, time-of-flight neutron diffraction and S-edge EXAFS. For the ultramarine yellow/green structure, Fig. 6, sulfur edge EXAFS has shown the S–S distance in the S_2^- ion to be 2.1 Å. In combination with low temperature powder neutron diffraction studies this distance is confirmed with the S_2^- dimers lining up along the cavity axis. The structure of ultramarine blue, $Na_{7.2}[AlSiO_4]_6{\cdot}(S_3)_{1.2}$, is rather more difficult to model due to the positional disorder in the trimeric polyanion with two distinct sulfur types. Through a joint sulfur edge EXAFS /powder diffraction analysis the S_3^- unit, with S–S 2.05 Å and S–S–S 110°, has been found to be displaced slightly from the β-cage centre, Fig. 6.

The trapping and stabilisation of an otherwise reactive anionic species in the sodalite cage, as seen with ultramarine, may be extended to other simple inorganic species. For example the permanganate ion can readily be trapped within the cavity, in $Na_8[AlSiO_4]_6(MnO_4)_2$,[29] and is stabilised to higher temperatures than in the free salt. The material is also non-oxidising unless the cage is removed, for example by (slow) dissolution in very strong acids. Chromate sodalite $Na_8[SiAlO_4]_6(CrO_4)$ is extremely thermally stable and might avoid the toxicity problems associated with free chromate(VI). This ability of the sodalite framework to isolate and thus stabilise otherwise reactive inorganic species has been extended to other species for example the BO_2^- unit[64] which is produced by partial thermal decomposition of $Na_{7.55}(AlSiO_4)_6(B(OH)_4)_{1.685}\ (H_2O)_{1.97}$.

Cancrinite

Cancrinite is a naturally occurring mineral, $Ca_2Na_6(AlSiO_4)_6$-$(CO_3)_2{\cdot}nH_2O$, that belongs to the chabazite zeolite sub-group which also contains sodalite, and is based on the stacking of six rings.[65] Sodalite is comprised of the six ring stacking sequence

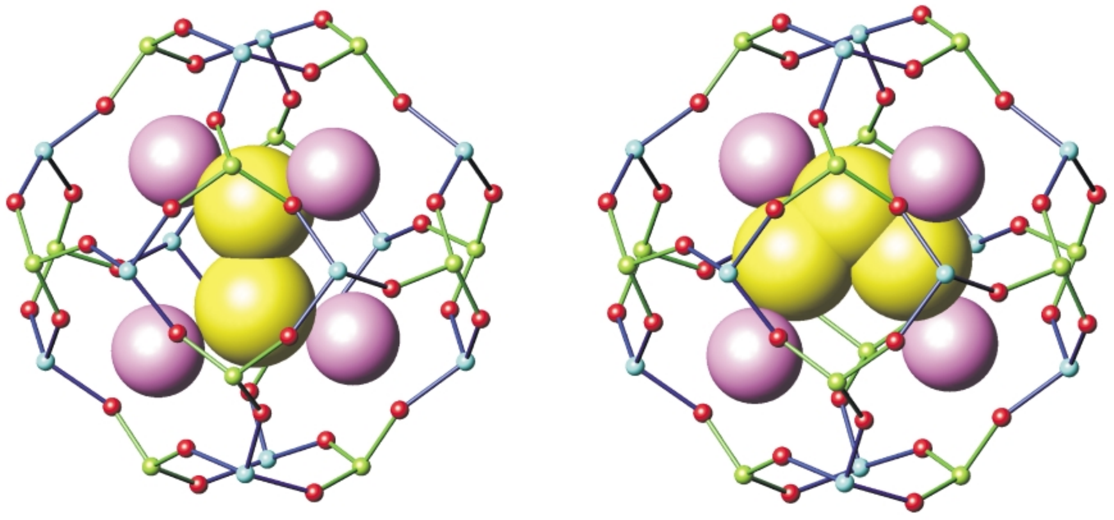

Fig. 6 The structures of the ultramarines yellow $Na_{6.7}[AlSiO_4]_6(S_2)_{0.67}$ and blue $Na_7[AlSiO_4]_6(S_3)$ derived from the analysis of S-edge EXAFS and powder neutron/X-ray diffraction data. Sulfur atoms are yellow, sodium ions magenta.

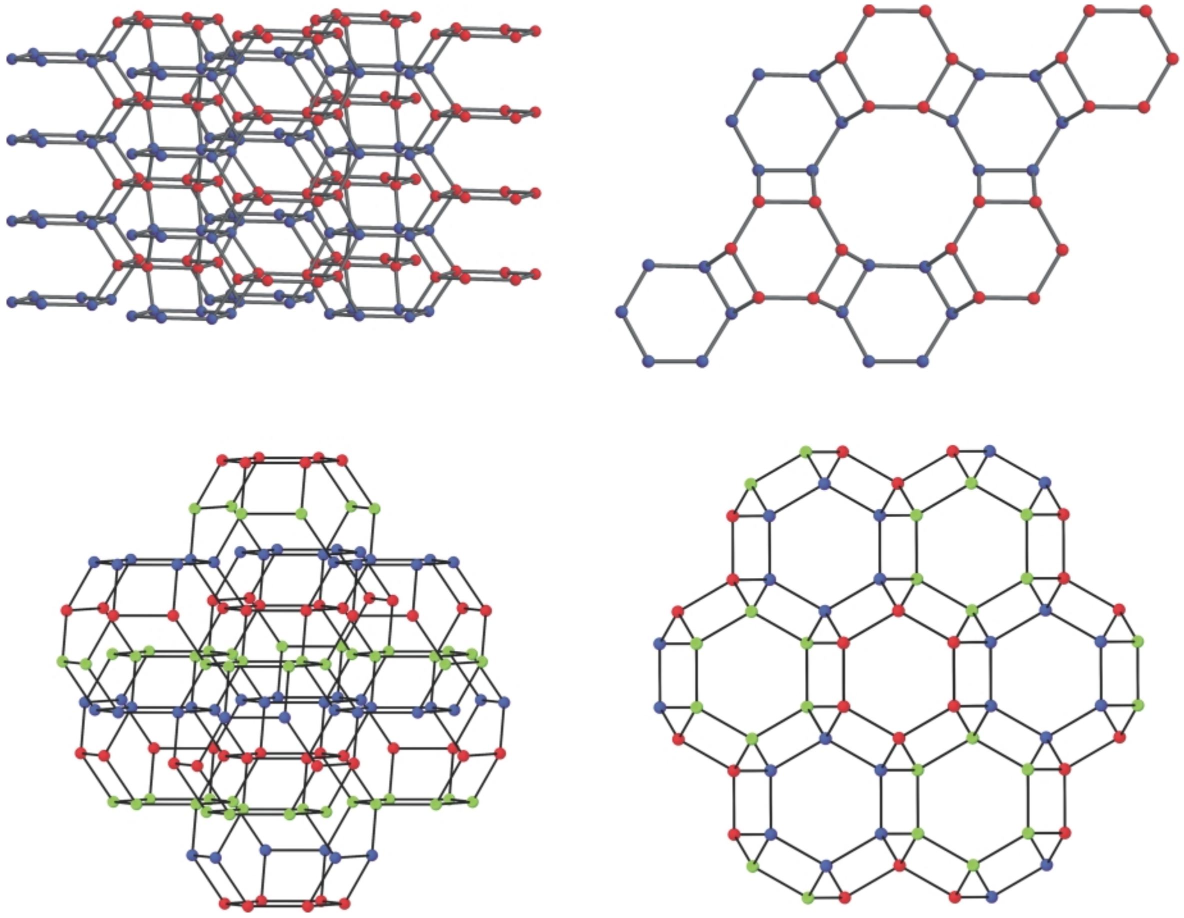

Fig. 7 The stacking sequence of 6-rings in the sodalite (ABCABC ..), bottom, and the cancrinite (ABABAB ....), top, structures and the derived pore structures (right). Tetrahedral atoms in the two structures are coloured red, green and blue to represent the different positions of the vertically stacked layers.

ABCABC, whereas cancrinite may represented as ABAB as shown in Fig. 7. The cancrinite structure is a common intergrowth in sodalite products, and can adopt the same general formula as a sodalite. Other related intergrowth structures include those of afghanite (ABABACAC stacking sequence of six rings) and liottite (ABABAC stacking sequence of six rings). The structure, shown in Fig. 8, is built up from 11-hedral cages and channels both surrounded by puckered twelve membered rings.[66] Water molecules reside in the channels and in the 11-hedral cages, anions in the channel centres, and, as in sodalites, the metal cations are located in the six ring windows and in the main channels.

Cancrinites can be synthesized under similar conditions to sodalites and the formation of one structure in preference to the other generally results from the symmetry of and charge on the enclathrated anions. Anions with a threefold rotation axis, such as nitrate and carbonate, generally direct the formation of the hexagonal cancrinite structure, while simple monatomic ions, *e.g.* Br^-, and those with lower symmetry, *e.g.* NO_2^-, generate sodalite frameworks. Tetrahedral species, for example sulfate, with cubic symmetry in addition to the threefold axis can template either structure. An additional factor is that divalent anions promote the formation of cancrinite possibly due to stronger interactions with cations yielding ion clusters with threefold symmetry which template the hexagonal structures. Such behaviour is seen clearly for the manganate and permanganate anions, the former yielding cancrinite[67] and the latter sodalite.[29]

Ion exchange of the non-framework cations can take place in the same way as for sodalites, as can intra-cage modification of the anions.[47] The structure can be converted into sodalite in some cases[68] by heating to approximately 800 °C, if the anion displays sufficient thermal stability. Since the structure is rather more open than that of sodalites, cancrinites are hygroscopic and are less thermally stable but access to and interactions between the anions is possible along the main channel. Redox reactions can also be carried out on the channel species, for example manganate cancrinite $Na_8(AlSiO_4)_6MnO_4\cdot nH_2O$ can be oxidised from solution to permanganate cancrinite $Na_7(AlSiO_4)_6\cdot MnO_4\cdot nH_2O$, which cannot be synthesized directly as the sodalite framework is normally templated by this ion.[29]

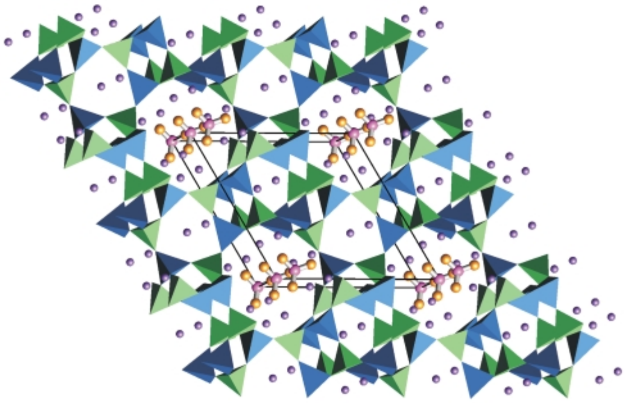

Fig. 8 Representation of the structure of manganate cancrinite $Na_8[AlSiO_4]_6MnO_4$ viewed down the main channel direction (*c*). The framework consists of tetrahedral units, with alternating Si (green polyhedra) and Al (blue polyhedra). The channels contain columns of manganate ions (tetrahedral units: manganese, magenta; oxygen, orange). Sodium ions (purple) are present in the main channels and 11-hedral cages. Water molecules are not shown for clarity.

The hydration of the cations in the cancrinite framework and its lower thermal stability, with ready conversion into sodalite, limit the chemical substitutions into the framework that have been achieved with this structure; synthesis has only been achieved from aqueous solution. Using hydrothermal routes aluminogermanate, gallosilicate and zincophosphate cancrinites have all been prepared. We have recently reported[46] a number of new members of this family including $Na_8[AlGeO_4]_6X$ ($X = WO_4^{2-}$, MoO_4^{2-}, CrO_4^{2-}, $S_2O_3^{2-}$ or $S_2O_5^{2-}$), $Na_8[GaSiO_4]_6X$ ($X = MoO_4^{2-}$, $S_2O_3^{2-}$, SO_4^{2-} or NO_3^{-}). No gallogermanate cancrinites have been reported, presumably as a result of the relative difficulty in forming the weaker Ga–O–Ge links from aqueous solution.

The one-dimensional channel of cancrinite containing both anions and cations can be considered as a infinite column of inorganic material of typical stoichiometry $[(M^+)_6X^{2-}]$ which in the hydrated form has a sheath of water. Chains of selenium atoms and Se_2 pairs have been grown in these channels.[69,70] However the cancrinite channels rarely grow perfectly with extensive stacking faults of the cages. This is seen in so-called disordered cancrinites or intergrowth structures such as afghanite, littoite and natrodavyne. For this reason the chains of inorganic structure that can be built in the cancrinite channels are severely restricted in length.

Tschoertnerite

Tschoertnerite,[71] IZA code TSC,[1] is a recently discovered zeolite mineral which is unusual in that it contains anions within the cages and has an extremely low framework density, Fig. 1. The structure consists of various cage types that contain either hydrated cations, calcium, potassium, strontium, and/or copper with hydroxide and chloride anions. It could be considered as being derived from mixed templating based on the normal hydrated cations plus simple inorganic material *i.e.* calcium copper hydroxide. This large trapped unit has the formula $[Cu_{12}(OH)_{24}]Ca_8O_{24}(H_2O)_8$ constructed from a rhombdodecahedron-like arrangement of corner sharing CuO_4 square planes and CaO_7 polyhedra. The sodalite cages, which also form part of this structure, contain $Ca_4O_4O_{12}$ units constructed from edge sharing CaO_6 octahedra in a tetrahedral arrangement.

While tschoertnerite is an extremely rare mineral its nature, as a very open framework structure seemingly partially templated around hydrated inorganic oxide/hydroxide moieties, indicates that significant opportunities exist to use solution stable inorganic agglomerates to template new framework structures.

The ABW structure type

The existence of zeolites in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system was first reported almost 50 years ago by Barrer and White[72] including the Li-ABW structure type, $LiAlSiO_4·H_2O$. However, the first structure determination of Li-ABW, using powder X-ray diffraction techniques, was achieved in the early seventies by Kerr.[73] The structure was later confirmed by single crystal X-ray diffraction studies[74] and the hydrogen (deuterium) positions determined from powder neutron diffraction studies.[75] The framework is built of corner sharing tetrahedral units with framework cation ordering in accordance with Löwensteins rule. The structure can be described as being made up of 4-, 6- and 8-membered rings (see Fig. 9), with the largest forming channels along the twofold screw axis, in Li-ABW the *c* axis. The Li^+ counter cation occupies sites within these channels along with the zeolitic water.

The ABW topology is widely adopted by inorganic compounds and a number of these structures have been tabulated.[76] The ABW structure can be formed using a broad array of chemical compositions and examples of systems with monovalent (T^+)/ hexavalent (T^{6+})[77,78] divalent (T^{2+})/ pentavalent (T^{5+})[79,80] and trivalent (T^{3+})/ tetravalent (T^{4+})[81,82] tetrahedral centres have been characterised with a monovalent counter cation (*e.g.* Group I, Tl^+ and NH_4^+ ions). Two fluoroberyllates have also been found to adopt this topology, further expanding the compositional limit of the structure type.[83,84] The highest symmetry that is found for the ABW type framework topology is *Imma*. However, to date only one example has been characterised, $CsAlTiO_4$;[85] in this case the framework cations Al and Ti are statistically disordered, probably a result of the similar ionic radii of tetrahedral Al^{3+} and Ti^{4+} (0.39 and 0.42 Å respectively).[86]

We have recently extended the ABW family further by introducing more unusual transition metal ions onto the tetrahedral sites, Table 2.[87,88] The stability of the ABW structure allows species that do not normally favour tetrahedral co-ordination to form a major component of the framework. Provided synthesis temperatures are kept reasonably low, through for example the use of gel precursor methods, then species such as $Co^{II}O_4$, $Fe^{III}O_4$, $Ti^{IV}O_4$ and $Ni^{II}O_4$ may adopt the ABW framework in combination with the more normal silicate and phosphate groups. Several of these are notable in terms of their composition; in $CsSiFeO_4$ the maximum level of iron has been reached for the first time in a zeolite structure. In $CsTiFeO_4$ and $CsTiAlO_4$, which also adopt the ABW structure, the titanium is a regular tetrahedral co-ordination and these framework structures contrast strongly with the titanosilicates obtained from aqueous solution which contain octahedral titanium.

Using similar synthesis methods we have also been able to incorporate the NiO_4 and CuO_4 units on to half the tetrahedral

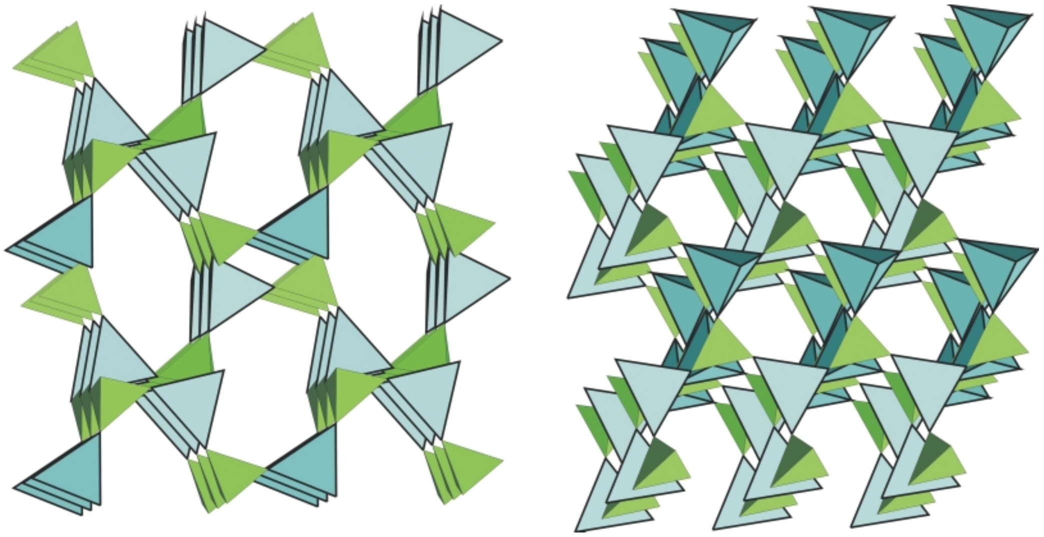

Fig. 9 The zeolite ABW framework constructed using alternating silicate (cyan) and aluminate (green) tetrahedra viewed along the *c* (left) and *b* (right) directions.

Table 2 Cell data and colour of some new framework substituted ABW structure types

Stoichiometry	a/Å	b/Å	c/Å	V/Å^3	Space group	Colour
$CsAlSiO_4$	9.4397(4)	5.4372(2)	8.8957(3)	456.58(4)	$Pc2_1n$	White
$CsAlTiO_4$	8.9811(4)	5.7351(3)	9.9548(4)	512.75(4)	$Imma$	White
$CsAlGeO_4$	9.4717(5)	5.4997(3)	9.2610(5)	482.42(5)	$Pc2_1n$	White
$CsGaSiO_4$	9.3294(2)	5.4293(1)	9.2450(2)	468.28(2)	$Pc2_1n$	White
$CsGaTiO_4$	9.1470(3)	5.7761(2)	9.9344(4)	524.87(3)	$Imma$	White
$CsFeSiO_4$	9.5858(4)	5.5538(3)	9.0476(4)	481.67(4)	$Pc2_1n$	Yellow
$RbNiPO_4$	9.28673	5.08216	8.93493	421.70(3)	$Pc2_1n$	Maroon
$CsNiPO_4$	18.5671	5.3543	9.0783	902.51(2)	$P2_1/a$ $\beta = 90.02°$	Blue
$CsCoPO_4$	18.4281(2)	5.4725(1)	9.2897(1)	936.82(1)	$P2_1/a$ $\beta = 90.365°$	Blue
$CsFeTiO_4$	9.9799(4)	5.8050(3)	9.1497(4)	530.07(4)	$Pc2_1n$	Brown

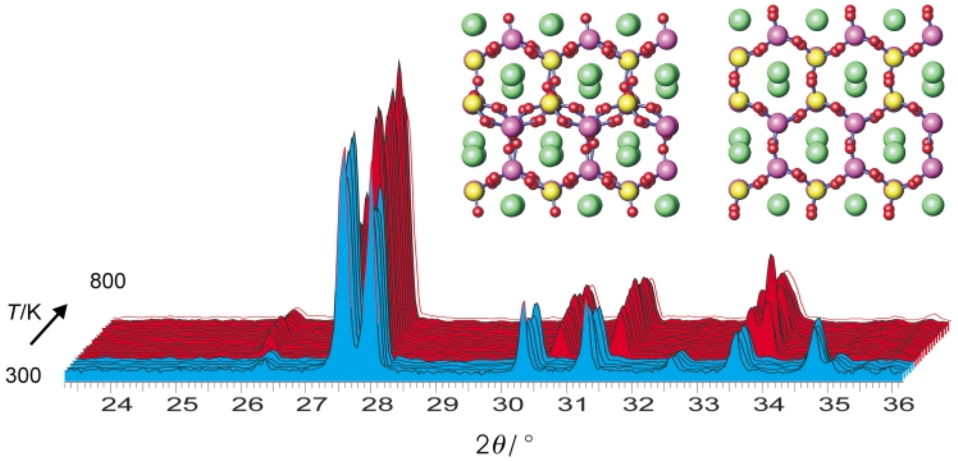

Fig. 10 Phase transition in the $CsCoPO_4$ ABW structure. Variable temperature powder X-ray diffraction data show a marked change in the pattern at 170 °C distinguished by the blue/red shading. The two structures viewed down the main channel are shown. Left: the low temperature form, space group $P2_1/a$, with a twisting of the TO_4 units in opposite directions with respect to each in successive layers. Right: the high temperature form, space group $Pn2_1a$.

sites in a zeotype structure for the first time. Previously these units had only been seen at low concentration in framework/oxide structures such as leucite, see analcime below. $RbNiPO_4$-ABW was obtained by heating a gel formed from a solution of nickel nitrate, ammonium dihydrogenphosphate and rubidium hydroxide at 750 °C. The material adopts the ABW framework as shown by refinement of powder neutron diffraction data, however the nickelate tetrahedron is severely distorted and a further oxygen can co-ordinate weakly to the nickel centre effectively increasing its co-ordination number. Such behaviour represents the tendency of nickel to increase its co-ordination geometry beyond tetrahedral in oxide structures; this behaviour can be seen in the other Group I nickel phosphates, for example the bright orange potassium nickel phosphate has five-co-ordinate nickel in square pyramidal geometry edge linked to phosphate groups, while yellow $LiNiPO_4$ has an olivine type structure with octahedral nickel. These light alkali metal nickel phosphates would clearly be classed as complex metal oxides. $RbNiPO_4$ represents an intermediate structure between that of $KNiPO_4$ and ABW and is maroon. $CsNiPO_4$ which is intense blue, the same as the leucite $Cs_2NiSi_5O_{12}$, presumably has a more regular NiO_4 tetrahedron but while this material has an ABW type framework framework disorder has prevented a full structure analysis. Very recently we have also succeeded in incorporating copper into an ABW framework structure, in $RbCuPO_4$ and the solid solution $Rb(Ni_{1-x}Cu_x)PO_4$. The former undergoes a structural transition between forms having four- and five-co-ordinate copper on the application of slight mechanical pressure.

The non-centrosymmetric nature of most of the compositions adopting the ABW framework indicates that these materials have potential applications as ferroelectric and non-linear optical materials. Many of these materials undergo phase changes as a function of temperature as a result of small rotations of the framework tetrahedra and displacements of the large alkali metal in the channel. We have recently observed a phase transition in $CsCoPO_4$ at 170 °C from the room temperature monoclinic form to a high temperature orthorhombic unit cell, Fig. 10. This occurs as a result of a regular rotation of the MO_4 tetrahedra along the c crystal direction, Fig. 10. Similar behaviour has been observed in $CsZnPO_4$[77] and NH_4LiSO_4.[79]

Replacement of silicon and aluminium in zeolite structures, particularly open frameworks, can have marked effects on their catalytic properties by providing redox centres and sites of modified acidity. This can be seen for gallium in a variety of zeolites, nickel in the MFI structure[89] and for iron in the sodalite structure.[90] The successful incorporation of high levels of such transition metal species onto the tetrahedral sites in a formal zeolite framework of the ABW type supports the belief that these species can form part of such frameworks as tetrahedral species and at signficant levels. In addition, substituted ABWs represent excellent models for the structures of doped zeolites in that the nature and geometry of the transition metal environment can be well defined, information that is difficult to achieve directly in substituted structures. For example the position of a dopant nickel atom in materials such as MFI[89] has been determined using EXAFS with a nickel environment consisting of four oxygens at 1.98 Å; this is in reasonable agreement with the nickel position in $RbNiPO_4$.

With high levels of paramagnetic transition metal species present in the framework a further possibility exists of correlated electronic effects between the centres. The magnetic properties of these new ABW frameworks summarised in Table 2 are currently being investigated. The separation of the metal centres by a phosphate or silicate tetrahedral unit will probably

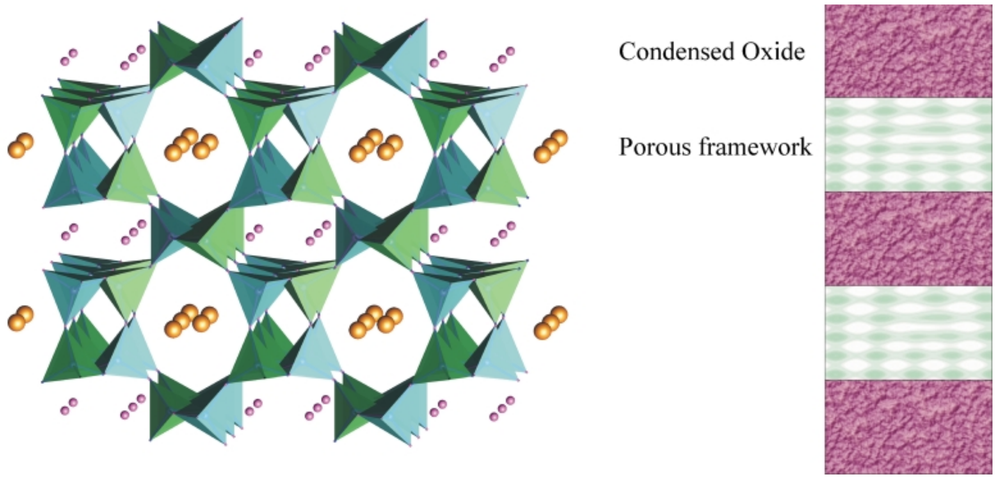

Fig. 11 The JBW framework of $Na_2Rb[Al_3Ge_3O_{12}]$ (left) viewed down the *c* direction showing the main 8-ring channels. The framework consists of alternating AlO_4 tetrahedra (cyan) and GeO_4 tetrahedra (green); sodium atoms are purple and rubidium gold. The schematic on the right represents the alternating layers of non-hydrated oxide (purple) and porous channels (green).

mean that these interactions will be weak and any long range ordering will only occur at low temperatures.

Zeolite JBW

Most zeolites are fully open in that the pores are directly connected by large channels separated by relatively thin aluminosilicate walls and small molecules, such as water, can be adsorbed into all sections of the structure. The zeolite JBW[91] is unusual in that a zeolitic portion of the structure is separated from the next by what is effectively a layer of the cristobalite structure containing non-hydrated cations,[5] Fig. 11. The existence of this semi-condensed block helps stabilise high aluminium contents and the JBW structure is invariably found for an Al : Si ratio of 1 : 1.

The JBW structure, first reported by Barrer and White in 1952,[92] is one of the less well studied zeolites; the crystal structure was solved (with the exception of a full description of the water molecules) in 1982 by Hansen and Fälth.[91] It was found to be orthorhombic with cell parameters $a = 16.426^{1}$, $b = 15.014^{5}$ and $c = 5.2235^{5}$ Å, $V = 1288$ Å^3, crystallising in the $Pna2_1$ space group. The crystals studied were grown hydrothermally at 200 °C from a sodium aluminosilicate glass in sodium hydroxide solution. However, the product formed under these conditions was multi-phase and the synthesis of pure bulk material with the JBW structure, $Na_2K[Al_3Si_3O_{12}]\cdot 0.5H_2O$, had not until recently[93] been described. In order to promote the formation of this phase, crystallisation from solutions containing *two* alkali metal ions is important, reflecting the two types of cavity present in the material. Non-hydrated sodium ions adopt positions in the semi-condensed cristobalite portion of the structure with co-ordination geometries to framework oxygen alone, Fig. 11. The larger hydrated potassium ions template the formation of the main 8-ring channels. The occupancy of the main channel formally consists of a linear array of alternating potassium ions and water molecules, though the true picture is probably complicated by slight variations in the level of hydration and the existence of incommensurate arrangements of potassium and their associated water molecules. However the approximate alternate ordering of potassium and water molecules along this crystallographic direction leads to a unit cell of twice the dimensions of the basic framework repeat.

We have recently adapted the JBW synthesis method described to allow isomorphous substitution of framework Si^{4+} and Al^{3+} for Ge^{4+} or Ga^{3+} respectively.[94] Zeolite $Na_2Rb[Al_3Ge_3O_{12}]\cdot 0.5H_2O$ AlGe-JBW, the first example of an aluminogermanate zeolite with the JBW structure, has fully been characterised by single crystal X-ray diffraction. The structure is slightly expanded from the aluminosilicate framework, $V = 1354$ Å^3, with strictly alternating AlO_4 and GeO_4 units in the framework, despite the similar size of Ge^{4+} and Al^{3+}. The thermal stability of the germanium substituted framework is reduced slightly from that of the aluminosilicate.

Caesium and rubidium, in combination with sodium, promote the formation of the JBW structure and, in particular, the 8-ring nature of the main channel which is common to both the ABW and JBW topologies. Hence the JBW structure with aluminosilicate and aluminogermanate frameworks can readily be formed for all with the cation combinations Na_2A where A = K, Rb or Cs. Both these ion types can be exchanged though the sodium ions are only replaceable by small cations such as lithium, hence ion exchange of $Na_2K[Al_3Si_3O_{12}]\cdot 0.5H_2O$ with lithium produces a fully exchanged material $Li_3[Al_3Si_3O_{12}]\cdot nH_2O$ while exchange with rubidium produces $Na_2Rb[Al_3Si_3O_{12}]\cdot mH_2O$.

The JBW structure offers a unique combination of structural features for a semi-condensed zeolite in that a hydrated pore structure is combined with a non-hydrated layer, which can be considered to be a section of complex oxide, shown schematically in Fig. 11. It might therefore be possible to combine the physical attributes of a complex oxide material such as electronic or magnetic properties with the porosity, particularly if the compositional flexibility of the ABW structure in terms of the introduction of transition metals can be incorporated into the framework.

Analcime (ANA)

One of the most compositionally flexible framework structures is that of analcime. The parent zeolite phase $Na_{16}[Al_{16}Si_{32}O_{96}]\cdot 16H_2O$ is cubic with irregular channels formed from very strongly distorted 8 rings, Fig. 12. Naturally occurring anhydrous derivatives of this framework type include pollucite $CsAlSi_2O_6$[95] and leucite $KAlSi_2O_6$[96] in which the hydrated sodium ion is replaced by the large alkali metal cation which is co-ordinated only to the framework oxygen ions. Leucite is cubic at high temperatures, above 605 °C, with 12 fold co-ordination to potassium but at lower temperatures distorts to a tetragonal form. Similar transformations are seen for other members of this family.

Substitutions into this structure have been achieved with a variety of metal ions, including Fe^{III}, Be, Mg, Co, Ni, Zn and Cu, using both dry solid state and hydrothermal methods.[97,98] Compositions recently reported include $Cs_2GeGa_2O_6$.[45] The structures of many of these have been refined from powder X-ray and neutron diffraction data. Most unusual are the nickel and copper containing frameworks $Cs_2MSi_5O_{12}$.[97,98] The transition metal is present at a fairly low level within the framework

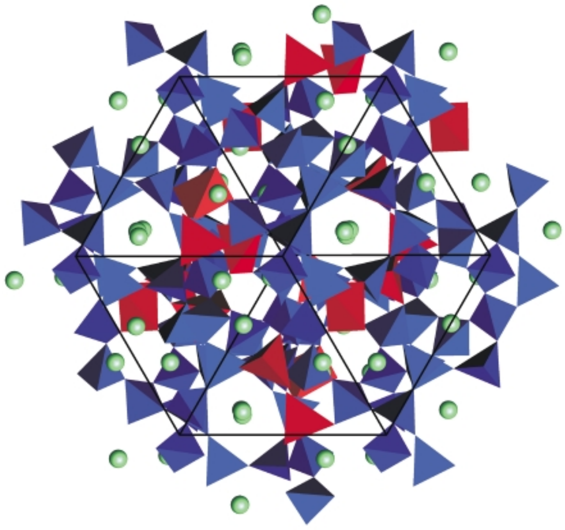

Fig. 12 The analcime (ANA) structure of $Cs_2MSi_5O_{12}$, M = Co or Ni, viewed down the main pore direction. The SiO_4 tetrahedra are shown in blue and MO_4 in red; caesium ions are green.

but orders on a portion of the tetrahedral sites in a fairly regular environment. $Cs_2NiSi_5O_{12}$ is a deep blue/violet while $Cs_2CuSi_5O_{12}$ is a paler sky blue colour.

The zeolite CAS and BIK frameworks

The zeolites with the CAS and BIK structure type codes have not been studied in detail. The CAS structure shown in Fig. 13 consists of 8-ring channels along the *c* lattice direction, separated by five membered rings.[99] This framework topology has only been seen for the anhydrous caesium aluminosilicate $Cs_4Al_4Si_{20}O_{48}$ (Araki[99]) and there is no report of this structure crystallising from aqueous solution. The density of this framework is higher than that of any other zeolite topology as a result of the high silicon content producing dense silica like regions and relatively few pores containing non-framework cations. The bikitaite framework also has 8-ring channels as the largest pores (Fig. 13) but this material is also known in a true zeolite form as $Li_2Al_2Si_4O_{12}{\cdot}2H_2O$[100] as well as the anhydrous caesium templated $CsAlSi_2O_6$.

Both the CAS and BIK structures would be ideal for framework substitutions with the same type of behaviour as has been achieved with, for example, the ABW structure. In terms of the channel species it should be possible to replace caesium in the CAS structure by $Li(H_2O)^+$ to produce a true zeolite though the conditions to form this high framework density material are likely to require the use of fairly high pressures, as required with BIK. More easily accomplished should be replacement of trivalent species within the framework by a transition metal generating materials such as CAS-$Cs_4Fe_4Si_{20}O_{48}$ or BIK-$CsCoSi_2O_6$ though materials of the latter composition seem to prefer to adopt the analcime framework.

Scapolites

The scapolites are a family of feldsparthoid minerals of the general formula $M_4[T_4O_8]X$ where M is an alkali metal, alkaline earth metal or mixture thereof, T represents varying levels of silicon and aluminium and X is an anionic species such as carbonate, sulfate or chloride. The end members of the main series of scapolites are marialite $Na_4Al_3Si_9O_{24}Cl$[101] and meionite $Ca_4Al_6Si_6O_{24}X$ with $X = CO_3$ or SO_4.[102] Intermediate stoichiometries such as $(Ca_{4.17}Na_{3.31}K_{0.46})(Si_{14.99}Al_{8.69})O_{47.8}$-$(Cl_{0.73}(SO_4)_{0.37}(CO_3)_{0.87})$[103] are often labelled as wernerite. The structure consists of a framework of linked SiO_4 and AlO_4 tetrahedra with cavities having a prolate spheroid shape containing the cations and anions, Fig. 14. As with the sodalite system it is possible to rewrite the formula as $[TO_2]_4^{3-}$ M_4X^{3+} and consider the structure as having square planar M_4X units embedded in the framework, Fig. 15. 8-Ring channels run through the structure along the *c* direction but these are very compressed to co-ordinate strongly the cations that they contain leaving little room for a hydration sphere. However in sarcolite, $Ca_6Na_{1.76}(Al_4Si_6O_{23})(OH)(H_2O)_{0.44}(SiO_4)_{0.25}(PO_4)_{0.25}$-$(CO_3)_{0.46}Cl_{0.04}$, a low level of hydration is associated with the calcium ions.[104]

Conclusion

Semi-condensed tetrahedral frameworks and related structures built from oxo-tetrahedra that incorporate anions within their frameworks form a compositionally very varied system. The framework species that form the tetrahedral unit MO_4 in zeotype structures has now been extended way beyond the well known period two elements Al, Si and P. The ABW structure is probably the most flexible with frameworks based on Ga, Ge, Be, As, Ti, Mg, Co, Zn, Fe, Ni and Cu all fully characterised. One (current) exception with the ABW framework is borate, BO_4, which is well known with sodalite and as a constituent in

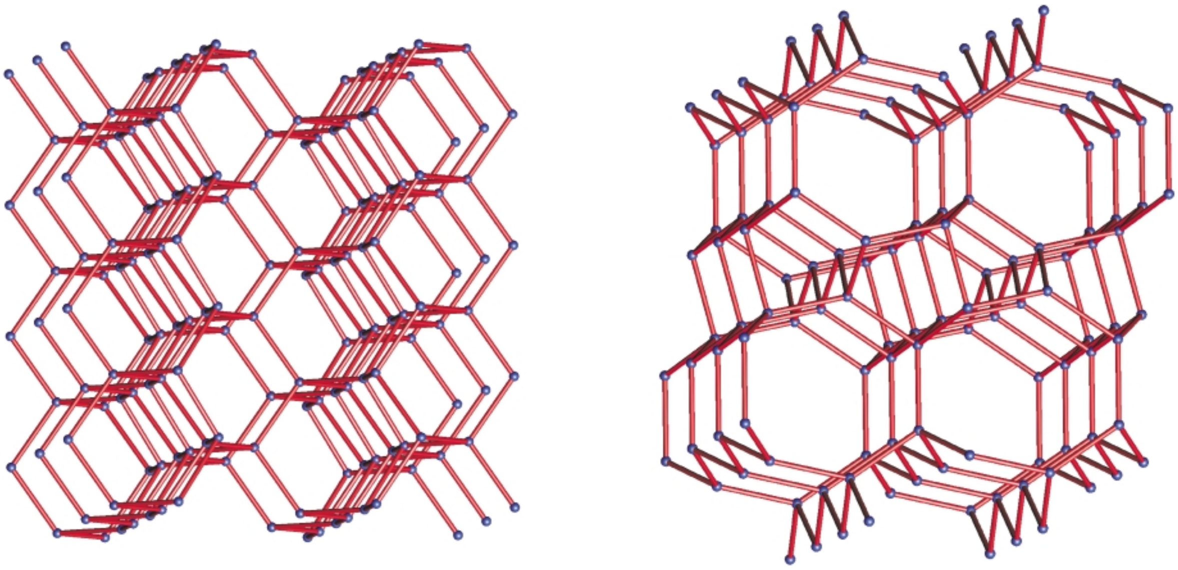

Fig. 13 The frameworks of the CAS (left) and BIK (right) zeolite structures. The framework oxygen atoms are not shown and the tetrahedral sites are linked directly.

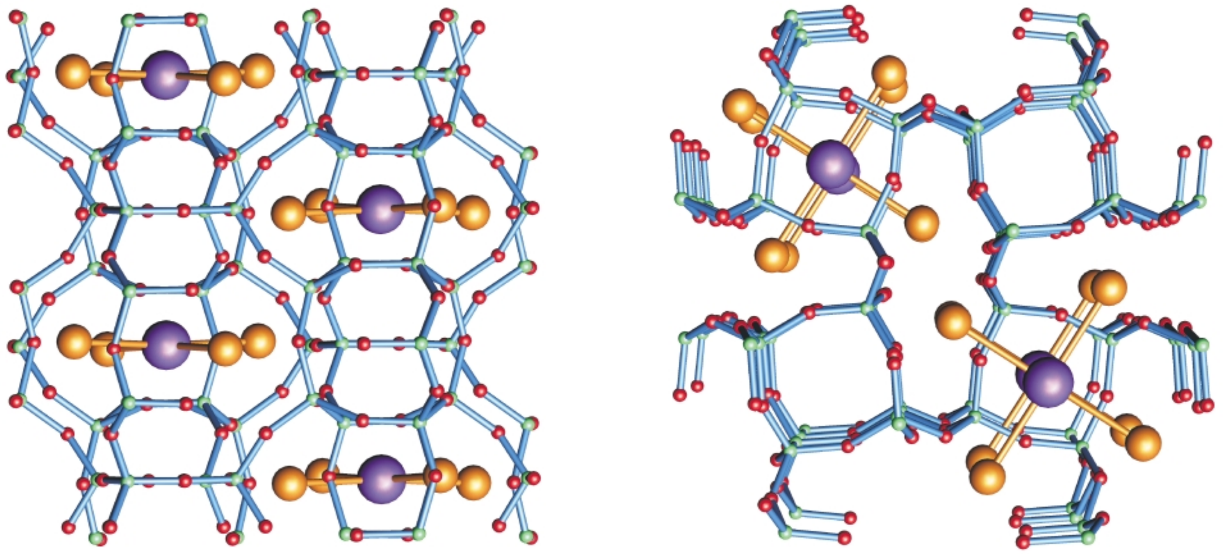

Fig. 14 The scapolite structure, $M_4[T_4O_8]X$, viewed down the *c* (left) and the *b* direction (right). The framework bonds are shown in blue, the anion (X) as the purple sphere and the cation (M) as gold spheres.

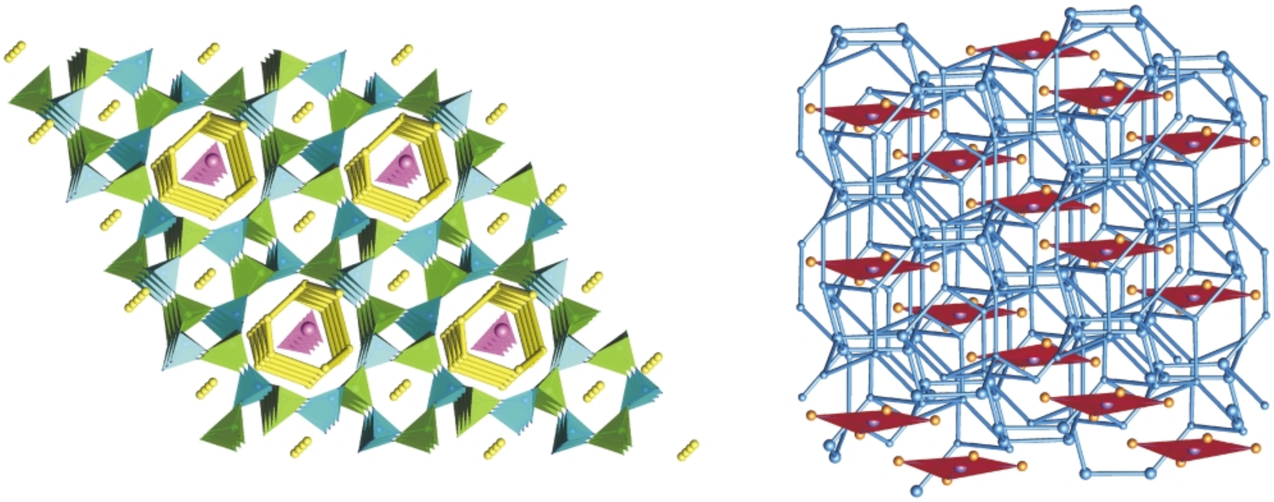

Fig. 15 Representations of the scapolite structure (right) showing the distribution of square planar M_4X units in three dimensions and cancrinite (left) showing triangular anions in the channels surrounded by the cations.

other zeolites. Incorporation of high levels of these species into other framework topologies will provide an exciting challenge. However the ready hydrolysis of these species and expansion of the co-ordination shell beyond four probably means that such synthesis will have to be undertaken under non-aqueous conditions.

One alternative view of the synthesis of these semi-condensed structures is that rather than hydrated cations templating the formation of the framework, large non-hydrated cations or ion clusters perform that role. For example the caesium ion performs much the same role as the hydrated lithium ion $Li(H_2O)^+$ in templating the structures of ABW and BIK. For the sodalite family the anhydrous ion cluster $[Na_4X]^{3+}$ takes the place of $M(H_2O)^{n+}$ in templating the sodalite cages in high temperature reactions. It would be interesting to extend this idea further and consider templating other structure types using larger ion clusters; the formation of tschoertnerite might indicate how such syntheses could be promoted.

Once the ion cluster has become incorporated into the framework the potential exists for generating arrays of simple inorganic units within the structure type. Not only can the composition and geometry of this unit be controlled but so can the separation and distribution pattern. So for example within the sodalite structure tetrahedral and cubic ion clusters can form into face centred and body centred arrays. By changing the framework composition and replacing aluminium and silicon by larger species such as germanium and gallium, the separation within the entrapped array is increased. The cancrinite and scapolite framework topologies with different distributions of pore geometries offer the potential to produce other arrays such as linked chains and stacked square planes.

Finally the JBW structure type represents a true hybrid layered oxide/zeolite structure with alternating channels and condensed non-hydrated oxide blocks. This material obviously has structural relationships with pillared clays[105] and the layered complex metal oxides of the type $CsNbTi_2O_7$.[106] The goals would be to combine the compositional flexibility of, for example, the ABW structure unit introducing a range of transition metal ions and/or develop new structures with alternative complex metal oxide layers interspersed with more open porous layers.

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