Russian Chemical Reviews **65** (4) 287 – 305 (1996)
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UDC 546.548

Design of inorganic compounds with tetrahedral anions

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Abstract. The review deals with aspects of the modelling of the compositions and properties of inorganic compounds with tetrahedral anions on the basis of crystal-chemical information. One of the possible algorithms employing crystal-chemical data for the modelling of the compositions, structures, and properties of new compounds is proposed on the basis of the structures of six structural types (glaserite, β-K_2SO_4, bredigite, palmierite, NASICON, and whitlockite). The likely usefulness of such data for the solution of various problems in materials science is demonstrated. The bibliography includes 208 references.

I. Introduction

Solid state chemistry is the science of chemical phenomena in solid materials observed during their preparation, heat treatment, use, ageing, and regeneration. This branch of chemistry is also concerned with the development of theoretical foundations for the synthesis of solid materials. Progress in many branches of science and engineering is determined by the development of new materials with a set of special properties. The methods of solid state chemistry have been devised to accelerate fundamental research involving the search for and development of new materials.

At the present stage of development, solid state chemistry faces a task concerned with the transition from the consideration of individual aspects of the structures, reactivities, and properties of materials with specified structures, properties, and compositions to the determination of the dependences of their properties on structure and the development of procedures for the construction of such materials based on scientific principles. This problem can be partly solved on the basis of crystal-chemical data and the theory of the electronic structure of solids and crystal lattice defects.

The employment of crystal-chemical data is of interest both for fundamental research — the understanding of the relations between the chemical compositions, structures, and properties of compounds — and for applied studies — the search for new materials with special and practically important properties (phosphors, chemical sensors, superconductors, catalysts, semiconductors, piezo- and ferro-electric materials, solid electrolytes, materials for the storage of information, etc.). The consideration of problems in materials science from the structure–property–composition standpoint makes it possible to achieve the specific syntheses of compounds and materials having specified physicochemical characteristics. However, problems in materials science have hitherto been usually solved by empirical methods. Such an approach retards the development of procedures for the synthesis of compounds possessing a set of predetermined parameters.

The structures of a large number of inorganic compounds (more than 15 000) have now been established. New studies concerned with the determination of the crystal structures of inorganic phases have mainly refined the assignment of a particular compound to a structural type already known. When the chemical composition of a compound becomes more complex, its subcell usually increases or becomes distorted, but the overall order in the alternation of cations and anions remains unchanged.

As an example, we shall consider the ideal structure of the natural mineral glaserite $K_3Na(SO_4)_2$ [space group (sp.gr.) $P\bar{3}m1$, $a = 5.680$ Å, $c = 7.309$ Å].[1] Following substitution in accordance with the scheme

$$Na^+ + 2SO_4^{2-} = R^{3+} + 2EO_4^{3-}$$

the compounds $K_3R(EO_4)_2$ (R^{3+} = rare earth, Y; E^{5+} = P, As, V) with a glaserite-like structure are formed.[2–4] Depending on the set of cations, different distortions of the ideal structure arise in the crystals — from trigonal in $K_3R(PO_4)_2$ (R = Sc, Lu)[5,6] to monoclinic in $R_3Nd(PO_4)_2$.[7] The characteristic features of such distortions have been discussed in a review.[8] Here we shall only note that the unit cell in lutetium and scandium compounds increases by a factor of 3 and in neodymium compounds by a factor of 2. A twofold increase in the size of the unit cell has been observed also in $K_2MR(PO_4)_2$ (M = Rb, Cs).[9]

Within the framework of the β-K_2SO_4 structural type (*Pnam*, $a = 7.456$ Å, $b = 10.08$ Å, $c = 5.776$ Å),[10] substitutions also occur, for example in accordance with the scheme

$$4K^+ + 2SO_4^{2-} \rightarrow 3Na^+ + R^{3+} + 2EO_4^{3-}$$

with formation of the compounds $NaR(EO_4)_2$.[11–15] They are subdivided into nine structural types,[16] each of them characterised by a different volume of the unit cell and a different space group. On passing from the ideal β-K_2SO_4

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Received 28 July 1995
Uspekhi Khimii **65** (4) 307 – 325 (1996); translated by A K Grzybowski

structure to structures of the type $Na_3R(EO_4)_2$, the volume of the unit cell increases by a factor of 1–6.[16] For other types of substitution, for example

$$2K^+ + SO_4^{2-} \rightarrow M^+ + M^{2+} + PO_4^{3-}$$

the size of the unit cell remains unchanged, as in $KBaPO_4$ (*Pnam*, $a = 7.709$ Å, $b = 5.663$ Å, $c = 9.972$ Å),[17] or increases, as in β-$CaNaPO_4$ ($Pn2_1a$, $a = 20.397$ Å, $b = 5.412$ Å, $c = 9.161$ Å),[18] depending on the radii of the cations forming part of the composition of the compounds.

In the examples quoted, the number of atoms in the subcell does not change and all the cationic sites are fully occupied, but it is possible to quote examples of structures in which some of the cationic sites may be vacant. For example, in the structures of $Ca_5(PO_4)_2SiO_4$,[19] $Cd_5(PO_4)_2EO_4$ (E = Ge, Si),[20] $NaCd_4(PO_4)_3$,[21] and α-$Ca_3(EO_4)_2$,[22] which are similar to that of β-K_2SO_4, one of the sites is partly occupied. The vacant sites in the crystal lattice may be occupied by additionally introduced cations and it is then possible to calculate theoretically the limiting compositions of the phases.

The stability of a structure with a partly occupied site (or sites) permits the existence of a lattice with a fully vacant site, i.e. it is possible to 'remove' from the lattice a calculated number of cations at non structure-forming sites and predict the limiting composition of the new phases. Consequently the formation and occupation of vacancies in the crystal lattice make it possible to model new compounds within wide composition ranges.

The arsenates, vanadates, and phosphates having the general formula $M_3(EO_4)_2$ (M = Sr, Ba; E = As, V, P)[24–27] and the molybdates $M_5R(MoO_4)_4$ (M = Rb, K, R = rare earth)[28–32] crystallise in the structural type of the natural mineral palmierite $K_2Pb(SO_4)_2$ ($R\bar{3}m$, $a = 5.49$ Å, $c = 20.83$ Å).[23] In most cases, these compounds retain the trigonal palmierite-like unit cell. A decrease of symmetry to monoclinic has been observed for some of them.[31] We emphasise that, among the numerous palmierite-like structures, there are no representatives with vacancies in the cationic sublattice.

As regards the modelling of new compounds with specified structures and properties, the NASICON (Na Super Ionic Conductor) structural type is of undoubted interest.[33] Compounds having the general formula $A_xM_2(EO_4)_3$, where A is a monovalent or divalent cation (Li^+, Na^+, K^+, Ag^+, Cu^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}), M is a divalent (Mg), trivalent (Sc, V, In, Cr, Fe), tetravalent (Ti, Zr), or pentavalent (Nb, Ta) cation, and E = Si, Ge, P, or As, and $0 \leqslant x \leqslant 4$, belong to this structural type.[34–38] In compounds of this class, the occupation of some of the cationic sites may vary from 1 [$x = 4$, $Na_4Zr_2(EO_4)_3$, E = Ge, Si][39,40] to 0 [$x = 0$, $Sc_2(MoO_4)_3$].[41] Depending on the set of cations, the symmetry of the unit cell varies from trigonal to monoclinic. It is also possible to quote examples of other isostructural classes of compounds with garnet,[42] perovskite,[43] bredigite,[44] eulythine,[45] and whitlockite[46] structures, in which some cations are substituted by others with retention of the overall architecture of the structure.

Many of the phases listed above were initially synthesised and only then assigned to a particular structural type, but most of them could be predicted within the framework of a definite structural type. All the necessary preconditions required for this purpose were in fact available, namely the crystal structures and radii of the cations were known[47,48] (in the present review the cationic radii quoted by Shannon[48] are used).

II. The use of crystal-chemical data for the construction of compounds with specified structures and properties

One example of the use of crystal-chemical data for the preparation of compounds in which the metal atoms would be in an unusual valence state is the synthesis of the La_2LiFeO_6 oxide phase containing Fe(V) cations.[49] The synthesis of this compound became possible by the creation of the necessary structural preconditions promoting the existence of the $t_{2g}^3e_g^0$ electronic configuration of the iron atoms. Demazeau et al.[49] stabilised the 'unusual' iron(V) valence state by introducing lithium cations, which strengthen the Fe–O bond by means of the six weakly competing Li–O bonds in the octahedron of the perovskite structural type.

Another example is the synthesis of the K_2NaPdF_6 fluoride phase.[50] The authors stabilised the palladium (III) ion in the $t_{2g}^6e_g^1$ electronic configuration, which is intermediate between the stable $t_{2g}^6e_g^0$ [Pd(IV)] and $t_{2g}^6e_g^2$ [Pd (II)] configurations, by the deformation of the elpasolite (K_2NaAlF_6) structural type. In the K_2NaPdF_6 lattice, the [PdF_6] octahedra are extended compared with the [AlF_6] octahedra, which also promotes stabilisation of the $t_{2g}^6e_g^1$ state.

After the discovery by Bednorz and Muller[51] of high-temperature superconductivity (HTSC) in the compounds $La_{2-x}Ba_xCuO_4$ with a perovskite-like structure, crystal-chemical data became the basis of the search for subsequent generations of materials with higher critical temperatures (T_c) of the transition to the superconducting state. The structures of the superconducting phases have been examined in detail in a number of reviews.[52–54] By selecting the ionic radii and the oxidation states of the cations within the framework of the perovskite structural type, the copper-containing superconducting oxide materials $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$,[55,56] $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$,[57,58] $Pb_2Sr_2R_xCu_3O_{8+\delta}$ (R = rare earth, Y; M = Ca, Sr),[59] and $HgBa_2CuO_{4+\delta}$ (see Ref. 60) were in fact synthesised. The conductivity in these phases is ensured by the two-dimensional (CuO_2) layers.

Many superconducting compounds have the composition $A_mM_2R_{n-1}Cu_nO_x$, where A = Bi, Tl, Pb, or Hg, M = Ba or Sr, R = Ca or rare earth, and $m = 1$ or 2. They are made up of (AO), (MO), (BO), and (CuO_2) layers alternating along the c axis of the unit cell. An increase in the number of (CuO_2) layers in one block of the structure (usually to three) leads to an increase in the critical temperature T_c. The problem of the synthesis of multilayered structures of the 'puff pastry' type arose in this connection. This can be achieved by means of a layer-by-layer arrangement of the 'dielectric' blocks and CuO_2 layers. However, a necessary condition for the formation of such structures is that the distances in different layers are commensurate. This is particularly important for the (CuO_2) and (MO) layers, where the ratio $d_{M-O}:d_{Cu-O}$ must be approximately equal to $\sqrt{2}$.[74] In the layered HTSC cuprates, where the distance d_{Cu-O} varies from 1.9 to 1.98 Å, the distance d_{M-O} should be 2.69–2.80 Å, i.e. the cations M may be Ba^{2+}, Sr^{2+}, and La^{3+}. Such crystal-chemical preconditions served as a basis for the construction of the mercury-containing compounds $HgBaRCu_2O_{6+\delta}$ (R = rare earth)[61] and of superconductors of a new class[60] with the record-breaking critical temperatures $T_c = 135–164$ K.

The dimensions of the polyhedra in the structure make it possible to predict the positions of the cations in the lattice and their mobilities. Thus, in the case of superionic conductors with the NASICON structure,[33,62–64] it is possible to show on the basis of structural information that decrease in the size of the structure-forming cation (M) hinders the migration of the mobile sodium ions within the channels of the structural framework. The corresponding weakening of ionic conductivity has been observed experimentally on passing from $Na_3Zr_2(SiO_4)_2PO_4$ ($\sigma_{300\,°C} = 0.2\ \Omega^{-1}\ cm^{-1}$)[33,62] to $Na_3MgZr(PO_4)_3$ ($\sigma_{300\,°C} = 0.16\ \Omega^{-1}\ cm^{-1}$) and $Na_3MnZr(PO_4)_3$ ($\sigma_{300\,°C} = 5.5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$).[38] The radii of the structure-forming cations with CN = 6(r_{VI}) are 0.72 Å for Zr^{4+}, 0.83 Å for Mn^{2+}, and 0.72 Å for Mg^{2+}. On substitution of the tetravalent cation by a divalent one, the channels within the structure decrease with a corresponding diminution of conductivity. An analogous increase in conductivity is observed in $Na_3M_2(PO_4)_3$ on increase in the radius of the cation M.

Cation	r_{VI}/Å	$\sigma_{570\,°C}/\Omega^{-1}\,cm^{-1}$	Ref.
Cr^{3+}	0.615	7.8×10^{-3}	65
Fe^{3+}	0.645	9.8×10^{-3}	65
Sc^{3+}	0.745	5.0×10^{-2}	66

It follows from the examples presented that information about the dimensions of the channels makes it possible to alter deliberately the conductivity in structures of the NASICON type. Thus the analysis of vacancies made it possible to discover channels in which the sodium cations migrated from their narrowest sites.[67-69] Later a similar scheme was also proposed in other investigations.[70-72]

A structure of the NASICON type has a high capacity in relation to metal cations. This promotes the formation of a large number of compounds of this structural type having different compositions but identical structures. In the lattice of the NASICON type with the crystal-chemical formula $A'A_3M_2(EO)_4)_3$ (E = P, As, Si, Ge), heterovalent and isovalent substitutions can be carried out at the A', A, M, and E sites. The occupations of the A' and A sites may vary from 1 [in $Na_4Zr_2(EO_4)_3$][39,40] to 0 [in $Sc_2(MoO_4)_3$].[41] Monovalent [Li, Na, K, Cu; $A^{I}M_2^{IV}(PO_4)_3$],[35-38,73-78] divalent [Ca, Sr, Ba, Cu; $A^{II}_{0.5}M_2^{IV}(PO_4)_3$],[79-82] and trivalent [Ln; $A^{III}_{1/3}M_2^{IV}(PO_4)_3$][83] cations can enter these positions. Tetravalent (Zr, Hf, Ti, Ge, Sn)[39,40,74-86] and trivalent [Sc, Cr, Fe, Ga, V, In; $A^{I}_3M^{III}(PO_4)_3$][65,67,68,80,87-89] cations can enter the M positions. These positions can also be occupied by cations with different valences, for example divalent and trivalent [M^{II} = Mg, Zn; M^{III} = Sc, Cr; $Na_{2x}M^{II}_{2x}Sc_{2-2x}(PO_4)_3$, $Na_{3+x}Cr_{2-y}Mg_z\cdot(PO_4)_3$],[37,90] trivalent and tetravalent [M^{III} = Cr, Fe, Ga, In, Tl; M^{IV} = Ti, Zr; $A^{II}M^{III}M^{IV}PO_4)_3$],[79,80] as well as tetravalent and pentavalent [$Nb^{V}Ti^{IV}(PO_4)_3$ and $Nb^{V}Nb^{IV}(PO_4)_3$][34,91] cations. The compositions of the compounds listed above have been modelled on the basis of crystal-chemical data. The introduction of cations with different sizes and in different oxidation states influences appreciably the mobility of the type A cations in the three-dimensional cavity framework.[65,66,92] The latter fact is important for the preparation of solid electrolytes with specified electrophysical characteristics.

The ability of the $\{[M_2(EO_4)]^{p-}\}_{3\infty}$ framework to retain the cations of one element in different oxidation states at an A site (for example Cu^+ (see Refs 93-95) and Cu^{2+} (see Ref. 82)) promotes the occurrence of reversible redox reactions ($Cu^{2+} + \bar{e} \rightleftharpoons Cu^+$),[96] which is a precondition for the application of these materials as catalysts, for example in the dehydrogenation of butanol.[97]

Yet another example of the synthesis of compounds with a specified structure by means of isovalent substitution based on crystal-chemical data is the synthesis of the compounds $M_2M'R(PO_4)_2$ having structures analogous to that of glaserite with M-M' combinations: potassium-rubidium, potassium-cesium, and rubidium-cesium.[6,9,98] In conformity with the crystal-chemical formula of the glaserite-like structure $X^{[12]}Y^{[10]}_2M^{[6]}(EO_4)_2$, the chemical composition of the compounds was chosen in such a way that the number of alkali metal cations with a larger radius is two times smaller than that of the alkali metal cations with a smaller radius. This relation was established on the basis of the number of $X^{[12]}$ and $2Y^{[10]}$ sites in the glaserite type structure.[1] According to the results of structural analysis, the alkali metal cation with the larger radius in the glaserite-type structure occupies the more capacious $X^{[12]}$ site. Depending on the set of alkali metal cations, different types of distortions of the glaserite structure occur in the compounds under discussion.

Analysis of the dimensions of the polyhedra and of their number in the β-$Ca_3(PO_4)_2$ structure,[99] which belongs to the structural type of the mineral whitlockite $Ca_{18.19}Mg_{1.17}\cdot Fe_{0.83}H_{1.62}(PO_4)_{14}$,[46] made it possible to model the new compounds $Ca_9(PO_4)_7$ (R^{3+} = Ln, Y, Bi, Sc, Cr, Fe, In),[100-103] $Ca_{10}M(PO_4)_7$ (M = Li, Na, K, Cu),[104,105] and $Ca_9MgM(PO_4)_7$ (M = Li, Na, K)[106] and to predict a wide region corresponding to the ternary phosphates in the $Ca_3(PO_4)_2-RPO_4-M_3PO_4$ systems.[107] Cations with different dimensions and oxidation states (from +1 to +4) form part of the composition of the whitlockite-type crystal lattice.

Analysis of whitlockite like structures made it possible to predict the occurrence of reversible redox reactions. Such reactions proceed without the destruction of the crystal lattice but with a change in the oxidation state of the transition metal cation. The reduction reaction is accompanied by the incorporation of a proton in the crystal lattice, while the oxidation reaction involves its elimination.[108-110] The corresponding reactions proceed in accordance with the following schemes:

$$Ca_9Fe^{III}(PO_4)_7 + 0.45\,H_2 = Ca_9Fe^{II}_{0.9}Fe^{III}_{0.1}H_{0.9}(PO_4)_7 \quad (1)$$

$$Ca_9Fe^{II}_{0.9}Fe^{III}_{0.1}H_{0.9}(PO_4)_7 + 0.225O_2 = Ca_9Fe^{III}(PO_4)_7 + 0.45H_2O \quad (2)$$

The materials in the crystal lattice of which reversible redox reactions take place may be used as catalysts,[111-115] intermediates for the two-stage oxidation of hydrogen,[116,117] and sensors.[118]

Crystal chemistry makes it possible to interpret successfully and to predict the formation of different phases in oxide systems exhibiting a complex polymorphism. Such compounds have valuable practical properties (luminescent, magnetic, ferroelastic, piezo- and ferro-electric, and catalytic), which are often successfully combined in a single material. The properties of such complex systems cannot be always predicted, but the use of crystal-chemical data makes it possible to solve successfully certain controversial problems.[119]

The $Ca_3(PO_4)_2-Ca_2SiO_4$ system is important in the processing of natural phosphate raw material and in the metallurgy of converter slags. The experimental data obtained by different authors[120-124] concerning the regions of existence of individual phases in the system are extremely contradictory and it has been possible to interpret them correctly only by employing data on the structures of the individual phases of the system.[125] Furthermore, crystal-chemical data made it possible to justify on a scientific basis the use of various additives in the formation of a charge for the preparation of phosphate fertilisers with the maximum solubility in 2% citric acid solution[110,125-130] and hence to avoid additional studies concerning the search for the optimum charge composition.

The examples quoted demonstrate that crystal-chemical data can be used effectively for the prediction of the compositions of new compounds with specified physicochemical properties.

III. Construction of compounds with a new composition

In the modelling of new phases on the basis of crystal-chemical data, analysis of the dimensions of the occupied and vacant polyhedra and of their number is important in the first stage. The outcome of such analysis is the crystal-chemical formula of an individual structure or structural type on the basis of which the composition of the possible phases may be predicted by means of iso- or hetero-valent substitutions, taking into account the formal valences and dimensions of the cations. In addition, the dimensions of the ions and polyhedra in this structure make it possible to predict the positions of the atoms in the lattices.

The characteristic features of the structures of a series of structural types with tetrahedral anions, which will be used for the modelling of the compositions of compounds with specified structures and properties, are discussed below. The generalised data, obtained as a result of such analysis, provide an algorithm for the modelling of new compounds and their properties.

1. The glaserite $K_3Na(SO_4)_2$ structural type

The glaserite structural type is common among inorganic salts with tetrahedral anions. Two types of columns directed along the $\bar{3}$ axis are differentiated in the glaserite crystal lattice (Figs 1 and 2): cationic (C) and mixed cationic-anionic (A). The A column is made up of alternating (EO_4) tetrahedra and YO_{10} polyhedra: $\ldots-YO_{10}-EO_4-YO_{10}-\ldots$ (Fig. 1) The cation in the Y position is surrounded by ten oxygen atoms: four of these are close (three belong to the face of a single tetrahedron, the fourth apical oxygen — on the $\bar{3}$ axis — belongs to another tetrahedron), while six are remote (the edges of three tetrahedra are disposed along the equator) (Fig. 3*b*). The coordination number of this site can be formulated as $Y^{[4+6]}$.

The C columns in the glaserite-like structures are made up of octahedra and dodecahedra: $\ldots-MO_6-XO_{12}-MO_6-\ldots$ The atom at the M site is surrounded by six oxygen atoms (one atom each from the six tetrahedra) and its coordination number can be formulated as $M^{[6]}$ (Fig. 3*d*). The atom at the X site is surrounded by six nearest oxygen atoms (one oxygen atom each from the six tetrahedra) and six more remote apical oxygen atoms and its coordination number can be specified as $X^{[6+6]}$ (Fig. 3*a*). The crystal-chemical formula for glaserite-like structures can be written as $X^{[6+6]}Y_2^{[4+6]}M^{[6]}(EO_4)_2$. The cations K^+ in the $K_3Na(SO_4)_2$ structure occupy the large $X^{[6+6]}$ and $Y^{[4+6]}$ polyhedra, whilst the cations Na occupy the $M^{[6]}$ polyhedra.

The two neighbouring cationic-anionic type A columns in the glaserite-like structures have different orientations of the EO_4 tetrahedra along the $\bar{3}$ axis [with the apical oxygen atoms pointing downwards or upwards (Fig. 1)]. Each type C column is surrounded by three type A columns, in which the tetrahedra are oriented in such a way that the apical oxygen atoms are directed downwards, and by three columns with tetrahedra in which the apical oxygen atoms are directed upwards (Fig. 2). The greatest amount of information about the positions of the tetrahedra and the cations is contained in the projection of the glaserite-like structure on to the $(1\bar{1}1)$ plane. Henceforth we shall compare layers which are arranged around this plane. The glaserite structure can be constructed from such layers, two neighbouring layers being displaced relative to one another by 1/2 of a translation along the *c* axis, while two neighbouring A columns in the layer have the opposite orientations of the tetrahedra (Fig. 1).

It follows from the analysis of the surroundings of the $X^{[12]}$, $Y^{[10]}$, and $M^{[6]}$ sites that in a glaserite-like structure[1] with the composition $M_3M'(EO_4)_2$ there are three large polyhedra ($X^{[12]}$ + $2Y^{[10]}$) and one small polyhedron ($M^{[6]}$). This structural type is characteristic of salts in which the large cation : small cation ratio is 3 : 1. This ratio as well as the dimensions of the cations

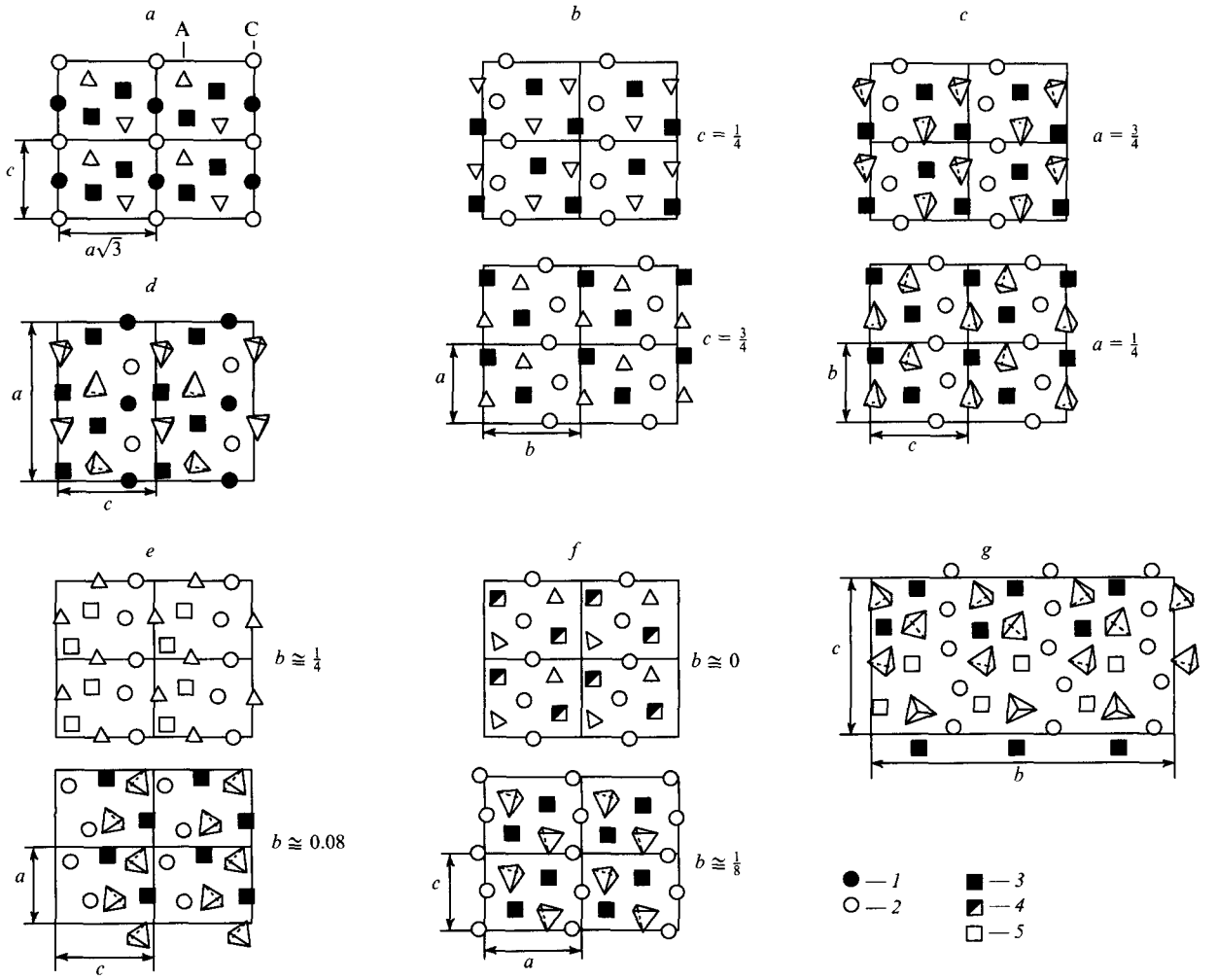


Figure 1. The layers in the $K_3Na(SO_4)_2$ and β-K_2SO_4 structural types.
(*a*) $K_3Na(SO_4)_2$; (*b*) β-K_2SO_4; (*c*) β-Ca_2SiO_4; (*d*) $Ca_3Mg(SiO_4)_2$; (*e*) $Ca_5(PO_4)_2SiO_4$; (*f*) $6\,Ca_2SiO_4 \cdot Ca_3(PO_4)_2$; (*g*) α-$Ca_3(PO_4)_2$.
Sites: (*1*) M = Na^+ or Mg^{2+} cations; (*2*) X = Ca^{2+} or K^+ cations; (*3*) and (*4*) Y = Ca^{2+} or K^+ cations.
(*3*) fully occupied site; (*4*) half-occupied site; (*5*) vacancy. The unit cells are differentiated. The triangles and tetrahedra represent anions.[125]

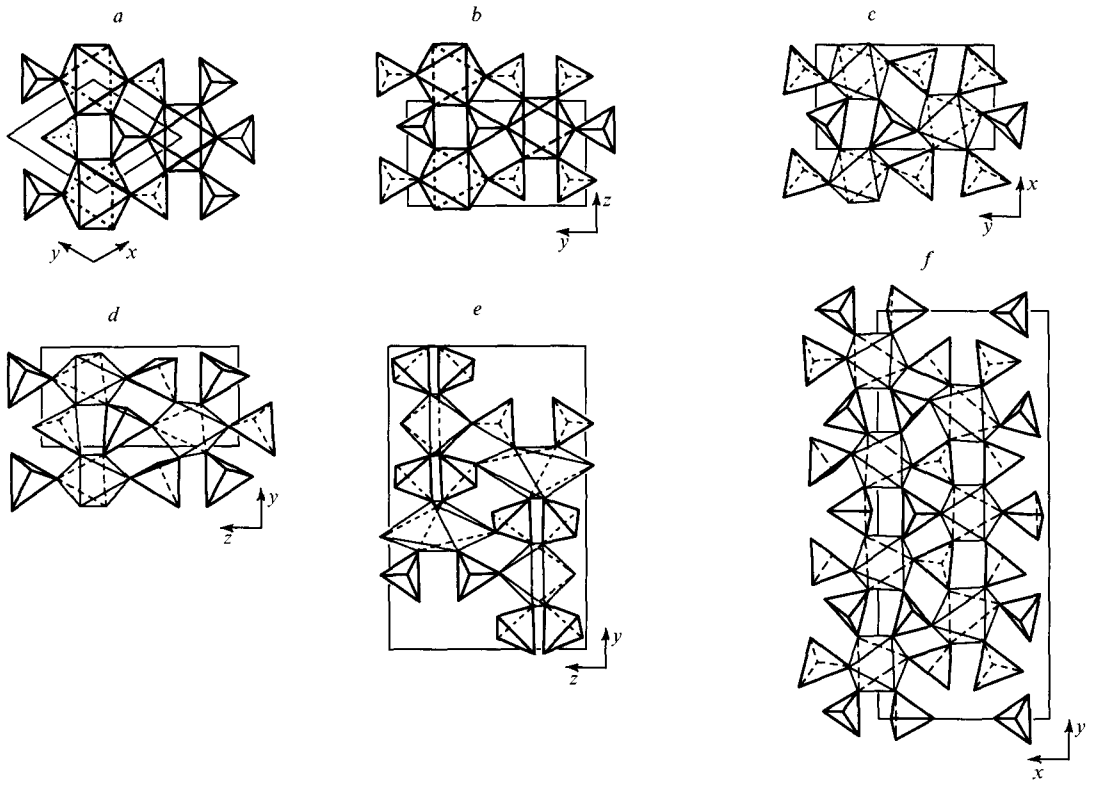


Figure 2. The alteration of polyhedra in the $K_3Na(SO_4)_2$ and β-K_2SO_4 structural types.
(*a*) $K_3Na(SO_4)_2$; (*b*) β-K_2SO_4; (*c*) β-Ca_2SiO_4; (*d*) $Ca_3Mg(SiO_4)_2$; (*e*) $Ca_5(PO_4)_2SiO_4$; (*f*) $6Ca_2SiO_4 \cdot Ca_3(PO_4)_2$. The unit cells are differentiated.[125]

are of fundamental importance in the formation of a glaserite-like structure. If the $K_3Na(SO_4)_2$ structure is adopted as a basis, then the difference Δr between the radii of potassium [$r_{XII}(K) = 1.64$ Å] and sodium [$r_{VI}(Na) = 1.02$ Å] is approximately 0.6 Å. In this case, an ideal arrangement is achieved. When this difference is altered (a set of other cations is adopted), the structure is distorted (Table 1). It may be metastable ($\Delta r = 0$) when the radii of the cations at the X, Y, and M sites are identical, as happens, for example, in α-Ca_2SiO_4 (see Ref. 131) and α′-$Ca_3(PO_4)_2$.[132] These two phases crystallise in the glaserite-like structural type and exist only at high temperatures. Under the usual conditions, they crystallise in the β-K_2SO_4 structural type,[10] which will be described below.

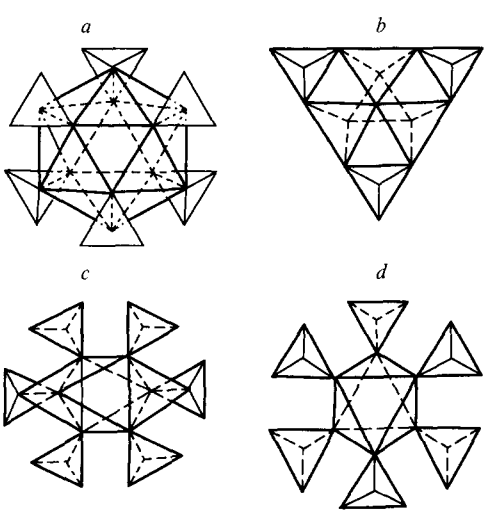


Figure 3. The $X^{[6+6]}$ (*a*), $Y^{[4+6]}$ (*b*), $X^{[6+3]}$ (*c*), and $M^{[6]}$ (*d*) polyhedra in the glaserite, palmierite, and β-K_2SO_4 structural types.[110]

With increase in the difference Δr, the symmetry of the cell may be reduced to monoclinic,[2] as happens, for example, in $Rb_3Sc(PO_4)_2$ [$r_{XII}(Rb^+) = 1.72$ Å, $r_{IX}(Sc^{3+}) = 0.745$ Å]. In this case, Δr has the maximum value of 0.97 Å among those known for glaserite-like phases. The minimum value $\Delta r = 0.59$ Å is observed for $BaNaPO_4$.[134] In the $Ca_3Mg(SiO_4)_2$ (merwinite) crystal lattice,[133] the positions of the tetrahedra are the same, apart from small rotations, as in the glaserite-like structure (Fig. 1). The Mg^{2+} cations occupy the M site, while the Ca^{2+} cations occupy the X and Y sites. Thus the partial replacement of Ca^{2+} by Mg^{2+} in calcium α-silicate leads to the formation of a stable glaserite-like structure.

The glaserite structural type is stable for compounds in which the difference between the radii of the cations occupying the M and X(Y) sites is in the range $0.59 \leqslant \Delta r \leqslant 0.89$ Å. With decrease in this difference, metastable glaserite-like structures or compounds crystallising in the β-K_2SO_4 structural type are formed.[10] The upper limit can apparently reach 0.98 Å. However, these data are unreliable, since the $Rb_3Sc(PO_4)_2$ structure, for which $\Delta r = 0.98$ Å, has not been investigated. In the case of cations with a small radius, characterised by an octahedral environment, the above difference Δr gives rise to the formation of the glaserite structural type. With increase in its radius, the small cation tends to increase the size of its coordination polyhedron and hence to alter the structural type. This conclusion can be well illustrated for compounds of the $K_3R(PO_4)_2$ series. Thus $K_3Lu(PO_4)_2$ (see Ref. 5) belongs to the glaserite structural type, whilst $K_3Nd(PO_4)_2$ (see Ref. 7) belongs to the β-K_2SO_4 structural type. According to Kalinin's data,[2] the glaserite structural type is stable for compounds with R = Gd–Lu.

It follows from the analysis of the distances in the polyhedra of the glaserite-like phases that the large cation : small cation ratio may also be 1 : 1. Thus a small cation, for example, sodium can also enter the $X^{[6+6]}$ position. Such a position of sodium (at the X and M sites) has been found in the crystal structures of $KNaSO_4$ (see Ref. 1) and $BaNaPO_4$.[134] Compounds with a

Table 1. X-Ray diffraction characteristics of certain glaserite-like phases.

Compound	a/Å	b/Å	c/Å	β/°	Space group	Δr/Å	Ref.
$K_3Na(SO_4)_2$ [a]	5.68	5.68	7.305		$P\bar{3}m1$	0.62	1
α-Ca_2SiO_4	5.529	5.529	7.311		$P\bar{3}m1$	0.0	131
$Ca_3Mg(SiO_4)_2$ [a]	13.254	5.293	9.328	91.90	$P2_1/a$	0.62	133
$K_3Sc(PO_4)_2$ [a]	9.430	9.430	7.629		$P\bar{3}m1$	0.89	6
$K_3Lu(PO_4)_2$ [a]	9.601	9.601	7.725		$P\bar{3}m1$	0.78	5
$Rb_3Sc(PO_4)_2$	10.51	10.07	9.813	104.6	—	0.97	2
$Rb_3Gd(PO_4)_2$	19.53	34.45	7.725	90.8	—	0.70	2
$Rb_3Ho(PO_4)_2$	9.879	9.879	8.118		$P\bar{3}m1$	0.70	2
$KNaSO_4$ [a]	5.607	5.607	7.177		$P\bar{3}m1$	0.62	1
$BaNaPO_4$ [a]	5.622	5.622	7.259		$P\bar{3}m1$	0.59	134

[a] The crystal structure has been determined.

similar composition have been found among tungstates and molybdates, for example $MR(EO_4)_2$ with M^I = K or Rb and R^{III} = Al, Sc, Fe, Cr, or In.[135] Thus the formation of the crystal lattice in the structural type under discussion depends both on the ratio of the radii of the cations and on their number.

Having at one's disposal data on the structure of $K_3Na(SO_4)_2$ and knowing the radii of the cations, it is possible to predict the compositions of a series of compounds which may crystallise in the glaserite structural type. Thus, the substitution of SO_4^{2-} by MoO_4^{2-}, EO_4^{3-} (E = P, V, As), and EO_4^{4-} (E = Si, Ge) and the selection of the corresponding cations in order to maintain electroneutrality may be expected to result in the formation of the compounds $M_3Na(MoO_4)_2$, $M'_3R(EO_4)_2$ (M' = K, Rb; R = Ln, Y, Sc; E = P, V, As), $M'_3M(SiO_4)_2$ (M' = Ba, Sr, Pb; M = Mg, Cu) and $BaCa_2Mg(SiO_4)_2$. Some of them have been described above. The characteristic features of the structures and the physicochemical properties of some of the glaserite-like phases have been described in detail.[2-6,8,9,79,135]

2. The β-K_2SO_4 structural type

The β-K_2SO_4 structure is made up of cationic (C) and cationic-anionic (A) columns (Fig. 1)[10] similar to the columns in the glaserite structure. In the type A column (...$-EO_4-YO_{10}-EO_4-$...), the coordination polyhedra are retained, whilst in the type C column (...$-XO_9-XO_9-$...) they are changed.

The cationic column in β-K_2SO_4 (see Ref. 10) is surrounded by four type A columns with a single orientation of the tetrahedron and by two such columns with a different orientation (Fig. 2). This results in the formation of a structure in which layers with a single orientation of the tetrahedra alternate with layers having tetrahedra with the opposite orientation (Fig. 1). In contrast to glaserite, in the structure of which two neighbouring tetrahedra from two type A columns always have the opposite orientations, in the β-K_2SO_4 structure the two neighbouring tetrahedra can have both identical or opposite orientations of the tetrahedra along the c axis of the unit cell (Fig. 1), i.e. on passing from glaserite to β-K_2SO_4 the orientation of some of the tetrahedra is reversed. As a result of the rotation of the tetrahedra, the unit cell symmetry is reduced from trigonal to orthorhombic, while the environment of the Y site in the A column is retained (Fig. 3*b*). The rotation of the tetrahedra in no way affects the positions of the E and Y sites on the threefold 'pseudoaxis', while the X site is displaced from this 'pseudoaxis'. The coordination numbers of the X and M sites in the C column are changed. These sites in the β-K_2SO_4 structure become equivalent and the immediate octahedral (as in glaserite) arrangement of the surrounding oxygen atoms from six tetrahedra is retained for these sites. When account is taken of the three more remote apical oxygen atoms, the coordination number of these sites (X and M) becomes nine — $X^{[6+3]}$ (Fig. 3*c*). The crystal-chemical formula of the β-K_2SO_4 structural type is $X^{[6+3]}Y^{[4+6]}EO_4$.

It follows from the analysis of the X−O and Y−O distances in the XO_9 and YO_{10} polyhedra that the β-K_2SO_4 structural type is more stable for cations with similar radii. Iso- and hetero-valent substitutions in the cationic and anionic sublattices of the β-K_2SO_4 structure may lead to compounds having different compositions. After the substitution of SO_4^{2-} by EO_4^{2-} (E^{VI} = Mo, W), EO_4^{3-} (E^V = P, V, As), and EO_4^{4-} (E = Si, Ge), it is necessary to select cations such that the ratio of their radii differs little from unity (Table 2). The formation of the β-K_2SO_4 structural type is promoted by cations tending to achieve an octahedral environment. The latter is associated with the fact that the X site in the must immediate environment must have six oxygen atoms (a distorted octahedron) and the long X−O distances in this octahedron promote the incorporation in the latter of cations with a radius greater than 0.9 Å.

β-Ca_2SiO_4 is constructed similarly to β-K_2SO_4.[136] The substitution of potassium by calcium and of SO_4^{2-} by SiO_4^{4-} is accompanied by a monoclinic distortion of the ideal β-K_2SO_4 structure. As can be seen from Fig. 2, on passing from β-K_2SO_4 to β-Ca_2SiO_4, the tetrahedra rotate and the reflection plane disappears. Owing to the rotation of the tetrahedra, eight oxygen atoms (one each from the six tetrahedra and two apical oxygen atoms) located at a distance of 2.36−2.80 Å, and a further one oxygen atom, separated by a distance of 3.25 Å, enter the first coordination spheres of the Ca^{2+} ions occupying the X sites. The coordination number of this site can be formulated as $X^{[8+1]}$. Furthermore, the rotation of the tetrahedra alters the immediate environment of the metal atom at the Y site: six oxygen atoms are accommodated in the first coordination sphere at distances of 2.30−2.75 Å, whilst the other four oxygen atoms, which build up the Y polyhedron to a decahedron, form the second coordination sphere with distances d_{Y-O} = 2.98−3.30 Å. The rotations of the tetrahedra also bring the two apical oxygen atoms closer to the Y site (d_{Ca-O} = 3.48 and 3.56 Å). In β-K_2SO_4 they are separated by more than 4 Å. The coordination polyhedron of the Ca^{2+} cations at the Y site in the β-Ca_2SiO_4 structure can be formulated as $Y^{[6+4+2]}$, whereupon the crystal-chemical formula assumes the form $X^{[8+1]}Y^{[6+4+2]}EO_4$. The idealised formula is $X^{[9]}Y^{[10]}EO_4$, as in the β-K_2SO_4 structure. The layers in the two structures are similar (Fig. 1).

The γ-, β-, α'_L-, α'_H- and α-polymorphic modifications have been observed for Ca_2SiO_4.[137] The characteristic features of the structures of the polymorphic calcium orthosilicate modifications have been described in detail.[131,138,139] The α'_H-Ca_2SiO_4 phase is isostructural with α'-Sr_2SiO_3[139] and α'-$Sr_{1.9}Ba_{0.1}SiO_4$.[140] and has a structure of the undistorted β-K_2SO_4 type. The α'_L-Ca_2SiO_4 structure is intermediate between β-Ca_2SiO_4 and β-K_2SO_4 and is apparently constructed similarly to the calcium silicophosphate $6Ca_2SiO_4 \cdot Ca_3(PO_4)_2$ with partially ordered layers.[141] The α'_H-Ca_2SiO_4 structure is similar to the undistorted β-K_2SO_4 structure. According to

Table 2. X-Ray diffraction characteristics of certain phases based on the β-K_2SO_4 structure.

Compound	a/Å	b/Å	c/Å	β/°	Space group	Δr/Å	Ref.
β-K_2SO_4 [a]	7.456	10.08	5.776		*Pnam*	0	10
β-Ca_2SiO_4 [a]	5.502	6.745	9.297	94.59	$P2_1/n$	0	136
β-Sr_2SiO_4 [a]	5.663	7.084	9.767	92.67	$P2_1/n$	0	140
α'_L-Ca_2SiO_4	11.18	18.92	6.832		*Pmcn*	0	131
α'_H-Ca_2SiO_4	5.63	9.52	6.85		*Pmcn*	0	139
α'-Sr_2SiO_4	5.682	7.09	9.773		*Pmnb*	0	131
α'-$Sr_{1.9}Ba_{0.1}SiO_4$ [a]	5.674	7.08	9.745		*Pmnb*	0	140
$6Ca_2SiO_4 \cdot Ca_3(PO_4)_2$ [a]	9.40	21.71	6.83		$Pnm2_1$	0	141
$Ca_5(PO_4)_2SiO_4$ [a]	6.737	15.508	10.132		*Pnma*	0	19
α-$Ca_3(PO_4)_2$ [a]	12.887	27.280	15.219	126.2	$P2_1/a$	0	22
β-K_2PO_3F [a]	7.543	10.16	5.933		*Pnam*	0	10
$Cd_4Na(PO_4)_3$ [a]	6.67	15.10	10.04		*Pnam*	0.05	21
$Cd_5(PO_4)_2SiO_4$ [a]	6.692	14.99	10.140		*Pnam*	0	20
$Cd_5(PO_4)_2GeO_4$ [a]	6.734	15.107	10.210		*Pnam*	0	20
$KBaPO_4$ [a]	7.709	5.663	9.972		*Pnam*	0.06	17
β-$CaNa(PO_4)_2$ [a]	20.397	5.412	9.161		$Pn2_1a$	0.16	18
$Na_3La(VO_4)_2$ [a]	5.582	14.240	19.42		$Pbc2_1$	0.196	11
$Na_3Nd(PO_4)_2$ [a]	15.874	13.952	18.470		$Pbc2_1$	0.143	13
$Na_3Er(VO_4)_2$ [a]	5.490	9.739	7.215	93.1	$P2_1/n$	0.04	14
$K_3Nd(PO_4)_2$ [a]	9.532	5.631	14.22	90.95	$P2_1/m$	0.387	7
$Na_3Nd(VO_4)_2$ [a]	29.14	5.574	14.22	91.4	*Cc*	0.143	12

[a] The crystal structure has been determined.

Kozak et al,[131] the $\alpha'_H \rightarrow \alpha$ polymorphic transition can occur as a result of the jump of the 'small' Si_4^{4+} cation from its tetrahedron to a neighbouring vacant tetrahedron, which ultimately appears as rotation of the tetrahedra. As a result of such a jump, the structure of α-Ca_2SiO_4 corresponds to that of the ideal glaserite. The cationic positions are fully occupied in the crystal lattices of all the polymorphic modifications of calcium silicates.

In the β-K_2SO_4 structural type, substitutions in both cationic and anionic components are possible. For example, the compound β-K_2PO_3F, isostructural with β-K_2SO_4, has been synthesised.[10] The structures of compounds with vacancies in the cationic sublattice, for example the calcium silicophosphates formed in the $Ca_2SiO_4-Ca_3(PO_4)_2$ system, have been described.[19,22,141]

Two crystal structures have been determined for calcium silicophosphates: $6Ca_2SiO_4 \cdot Ca_3(EO_4)_2$ (see Ref. 141) and $Ca_5(PO_4)_2SiO_4$.[19] The $6Ca_2SiO_4 \cdot Ca_3(PO_4)_2$ structure belongs to the β-K_2SO_4 structural type. Four-layer fragments along the [010] direction can be differentiated in it (Figs 1 and 2). Three layers are the same as in the β-Ca_2SiO_4 structure, whilst the fourth layer differs little from the layer in β-K_2SO_4. A similar alternation of distorted and undistorted (weakly distorted) layers has been found in $Cd_5(PO_4)_2EO_4$ (E = Si, Ge),[20] $Cd_4Na(PO_4)_3$,[21] and α-$Ca_3(PO_4)_2$.[22] We may note that the Y sites in the undistorted layer of these structures are vacant. Taking into account the latter factor, one may claim that the Y sites in the $6Ca_2SiO \cdot Ca_3(PO_4)_2$ structure are half-occupied in one layer (Fig. 1), while in the remaining layers they are still fully occupied (Fig. 2). This structure can be obtained by the alternation of the three occupied layers and one layer with a half-occupied site. The coordination numbers of the Y site vary from 7 to 10, whilst those of the X site are 7 and 8.

The structure of silicocamotite $Ca_5(PO_4)_2SiO_4$ can also be built up by alternating the layers (two with a occupied Y site and one with an vacant Y site) (Figs 1 and 2).[19] The two occupied layers resemble in this instance the analogous layers in β-Ca_2SiO_4, while the layer with an vacant Y site corresponds to the layer in the β-K_2SO_4 structure. Appreciable rotation and shifts of the tetrahedra from the ideal sites are observed in the occupied layers, whereas in the vacant layer the vacancies in the type A column promote the 'ideal' arrangement of the tetrahedra.

The maximum distortion of the type β-K_2SO_4 lattice is observed in α-$Ca_3(PO_4)_2$.[22] An ordered occupation of the Y sites in type A columns occurs in this structure (Fig. 2). The tetrahedra in this structure are intermediate between the ideal positions in the β-K_2SO_4 and the glaserite structures. This is manifested also in the coordination numbers of calcium, which vary from 6 to 10. The intermediate structure α-$Ca_3(PO_4)_2$ has also been confirmed by the arrangement of the cations in the type C column, where some of the calcium cations are located virtually on the threefold 'pseudoaxis', whilst the others are arranged as in β-K_2SO_4 (Fig. 1).

At a temperature above 1723 K, the α-$Ca_3(PO_4)_2$ phase undergoes a transition to the α'-modification.[132] One may postulate that this modification is built up on the basis of the glaserite and not the β-K_2SO_4 structure. This conclusion was confirmed by the fact that a continuous series of solid solutions is formed at high temperatures (>1723 K) between α-Ca_2SiO_4 and α'-$Ca_3(PO_4)_2$,[120–123] which is possible only when the components of the system are isostructural.

It follows from the data presented that the β-K_2SO_4 structural type is more stable also in the presence of vacancies in the cationic sublattice. These vacancies are present only in the mixed anionic-cationic column (the Y site).[22,141] The maximum number of vacancies occurs in α-$Ca_3(PO_4)_2$.[22] In the α-$Ca_3(PO_4)_2$ lattice, the Y site is half-occupied. In the compounds $Cd_4Na(PO_4)_3$ (see Ref. 21) and $Cd_5(PO_4)_2EO_4$ (E = Si, Ge),[20] there is an intermediate occupation of the Y site, as in the case of $Ca_5(PO_4)_2SiO_4$.[19] The different degrees of occupation of the Y sites in these phases are clearly reflected by their crystal-chemical formulae: $X_2Y\square(PO_4)_2$ and $X_3Y_2\square(EO_4)_3$

With increase in the number of vacancies in the crystal lattice, the distortion of the type β-K_2SO_4 structure increases and in the silicophosphates the following features are observed: (1) the layers in which the Y sites are vacant or are partly occupied correspond to the ideal layers in β-K_2SO_4 (Figs 1 and 2); (2) neighbouring layers with fully occupied Y sites are distorted owing to the rotation of the tetrahedra. The individuality of the cation exerts a lesser influence on the crystal lattice. Thus $Cd_4Na(PO_4)_3$ (see Ref. 21) and $Ca_5(PO_4)_2SiO_4$ (see Ref. 19) have identical structures although they have different

sets of cations, but the degree of occupation of the Y sites is the same.

The distortion of the type β-K_2SO_4 structure is mainly associated with the rotation of the tetrahedra, which has been confirmed by luminescence spectroscopic studies of solid solutions in the $MNaPO-Na_2Eu(PO_4)_2$ (M = Ca, Sr) systems.[142,143] The authors note that the broadening of the lines in the luminescence spectra is associated with the rotation of the PO_4^{3-} tetrahedra without change in the cationic sublattice. The X-ray diffraction patterns of solid solutions in the $MNaPO-Na_2Eu(PO_4)_2$ (M = Ca, Sr) system are identical. On the other hand, three (for M = Ca) and two (for M = Sr) composition ranges with identical spectra have been differentiated in the luminescence spectra of these solid solutions.

Heterovalent substitution in accordance with the scheme

$$2K^+ + SO_4^{2-} \rightarrow M'^{+} + M^{2+} + PO_4^{3-}$$

leads to the formation of the compounds $M'MPO_4$ (rhenanites). There are data on the crystal structures of the compounds γ-, β-, and α-$NaSrVO_4$,[144] $NaBaPO_4$,[134,135] $KBaPO_4$,[17,146] $TlBePO_4$,[147] and β-$CaNaPO_4$.[18] Only the crystal structures of $KBaPO_4$ and β-$CaHaBO_4$ are of the β-K_2SO_4 type. In these structures, the alkali metal cations occupy the Y site, while the alkaline earth metal cations occupy the X site (Fig. 4). In the β-$CaNaPO_4$ structure, the type A column contains three different PO_4^{3-} tetrahedra. This increases the parameter *a* by a factor of three compared with that in β-K_2SO_4. As a result of the rotations of the tetrahedra in this structure, the coordination numbers of the Y and X sites change. In the β-$CaNaPO_4$ structure, the sodium cation is surrounded by six oxygen atoms in the immediate vicinity (up to 2.8 Å) or by ten oxygen atoms when more remote ones (up to 3.3 Å) are taken into account. The d_{Ca-O} distances in the cationic C column are 2.39–2.79 Å. The coordination polyhedron consists of eight oxygen atoms.

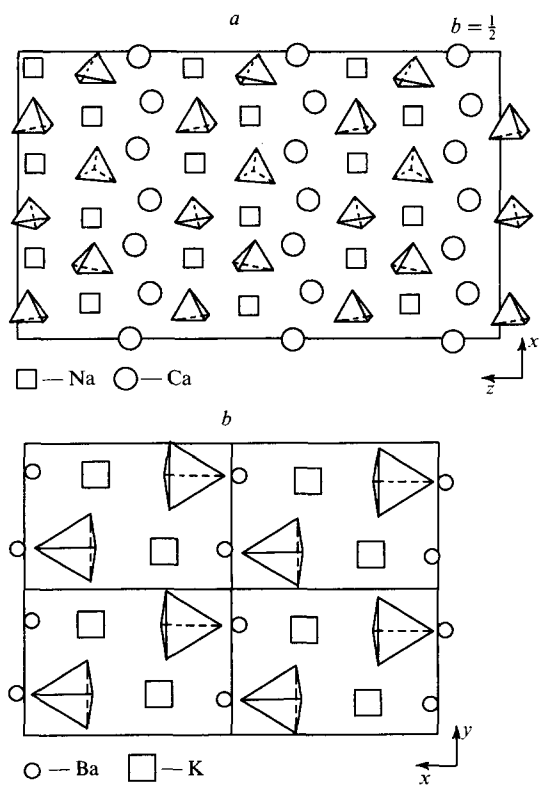


Figure 4. The layers in the β-$CaNaPO_4$ (*a*)[18] and $BaKPO_4$ (*b*)[17] structures.

As noted above, a large group of compounds with the composition $Na_3R(EO_4)_2$ (R = rare earth; E = P, V, As) crystallises in the β-K_2SO_4 structural type. Eight varieties of this structural family are distinguished (Fig. 5).[16]

The cations alternate in the same sequence in the compounds $Na_3R(EO_4)_2$. The lanthanide and sodium cations occupy the X site in an ordered manner (...–Na–R–Na–...). The Y site is occupied by sodium cations. Depending on the set of elements in the compounds, the crystal lattice is subjected to different distortions induced by the rotation of the EO_4 tetrahedra. The coordination polyhedra of the cations change as a result of the rotation of the tetrahedra (6–7 for Na, 6–8 for R). The rotation of the tetrahedra is induced by the tendency of sodium and lanthanide cations to assume smaller and larger coordination numbers respectively than those 'inherent' in the ideal β-K_2SO_4 structure.

It is noteworthy that the distortions of the crystal lattice in the compounds $Na_3R(EO_4)_2$ become more pronounced with increase in Δr (Table 2). For $Na_3R(PO_4)_2$ with R = Tm, Yb, or Lu, the structural type under discussion does not occur owing to the tendency of the lanthanide cations at the end of the series to acquire an environment comprising six oxygen atoms. The high-temperature modifications of $Na_3R(PO_4)_2$ (R = Tm–Lu)[148] crystallise similarly to the NASICON structural type.[73]

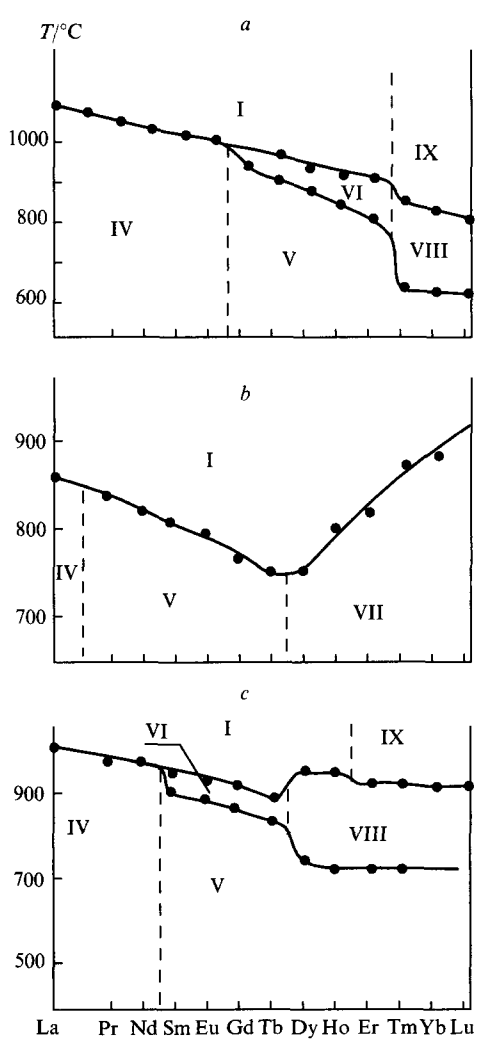


Figure 5. The regions of existence of the $Na_3R(EO_4)_2$ modifications, where E = P (*a*), V (*b*), As (*c*).[16]

The β-K_2SO_4 structural type is very common among phosphates, silicates, arsenates, and vanadates. The existence of a β-K_2SO_4 type structure with and without vacancies gives rise extensive possibilities for substitution in the cationic and anionic groups without a reconstructive rearrangement of the structure. The compositions of compounds with the β-K_2SO_4 structure may include monovalent, divalent, and trivalent cations. Thus, one may expect the formation of the silicates $MRSiO_4$ (M = Na, K), the phosphates $MCa_4(PO_4)_3$ (M = Na, K), and other phases. Laborious studies on phase diagrams are not needed in this instance. For example, the existence of the compounds $NaPbPO_4$, $NaPb_4(PO_4)_3$, $AgPbPO_4$, and $AgPb_4(PO_4)_3$ could have been postulated also without studying the phase diagrams for the $Na_3PO_4-Pb_3(PO_4)_2$ and $Ag_3PO_4-Pb_3(PO_4)_2$ system.[149] Quarton et al.[149] assigned the compounds $MPbPO_4$ (M = Na, Ag) and $MPb_4(PO_4)$ which they synthesised, to the β-K_2SO_4 and apatite structural types with vacancies respectively, but the unit cell parameters of all the compounds synthesised do not differ from the analogous parameters for potassium sulfate. Apparently the assignment of the compounds $MPb_4(PO_4)_3$ to the apatite and not the β-K_2SO_4 structural type should be regarded as erroneous, since, in view of the lack of $MPb_4(PO_4)_3$ single crystals, it was impossible to carry out a full X-ray diffraction study of these compounds.

As mentioned above, the β-K_2SO_4 structural type is stable for the compounds in which heterotypical cations (two or more) have similar radii. Such a structure obtains for the compounds $Na_3R(PO_4)_2$ (R = La–Ho),[13,14] $CaNaPO_4$,[18] and $KBaPO_4$.[17] With increase in the difference between the radii of heterotypical cations, the glaserite-like structure, of the kind occurring, for example, in $BaNaPO_4$ (see Ref. 134) and $KNaSO_4$,[1] or the olivine structure, as in $NaMnPO_4$ (see Ref. 150) and $NaB^{II}PO_4$ (B^{II} = Co, Fe, Mn, Gd),[151] becomes more stable. The features noted above, must be taken into account in modelling the compounds within the framework of the β-K_2SO_4 structural type.

3. The bredigite structural type

In the analysis of the structures of various modifications of $Na_3R(EO_4)_2$, there are difficulties in the assignment of the compounds to the β-E_2SO_4 or glaserite structural types. This applies particularly to compounds with large unit cells (Table 2). In such compounds, the tetrahedra have appreciably rotated away compared with the ideal arrangement. Some of them occupy, as it were, an intermediate position between their positions in glaserite and β-K_2SO_4. For an appropriate selection of the cations, one can apparently expect the formation of a phase with a 'mixed' (glaserite and β-K_2SO_4) arrangement of the tetrahedra. The compositions of such compounds should include small (<0.8 Å), medium (~1 Å), and large (>1.2 Å) cations.

Analysis of the literature data showed that such a compound does indeed exist and its composition corresponds to the general formula (Ca, Ba, Mn)$Ca_{13}Mg_2(SiO_4)_8$ (the mineral bredigite). The crystal structure of $Ca_{26.9}Ba_{0.6}Mg_{3.6}Mn_{0.9}(SiO_4)_{16}$ has been determined (space group *Pmch*, a = 10.909 Å, b = 18.34 Å, c = 6.739 Å, Z = 2).[44] The projections of the ideal and real structures of bredigite are presented in Fig. 6. This structure is made up of type A and C columns, as in β-K_2SO_4 and glaserite discussed above. The ideal crystal-chemical formula of the bredigite structural type, i.e. $X^{[12]}X_2^{[9]}Y_4^{[10]}M^{[6]}(EO_4)_4$ includes the polyhedra of the glaserite and β-K_2SO_4 structures in proportions of 1 : 2.

In the $Ca_{26.9}Ba_{0.6}Mg_{3.6}Mn_{0.9}(SiO_4)_{16}$ structure, there are two set of independent sites, two sites in each set, namely $X^{[12]}$ and $X^{[9]}$ in one set and $Y^{[10]}$ and $M^{[6]}$ in the other. The cations are distributed among the sites in the following manner:[44] X(1) = $0.707Ca^{2+} + 0.293Ba^{2+}$; M(1) = $0.93Mg^{2+} + 0.07Mn^{2+}$; Y(1) = $0.88Ca^{2+} + 0.12Mg^{2+}$. The remaining sites are occupied by calcium cations. Owing to the rotations of the tetrahedra (Fig. 6), in the real structure the coordination

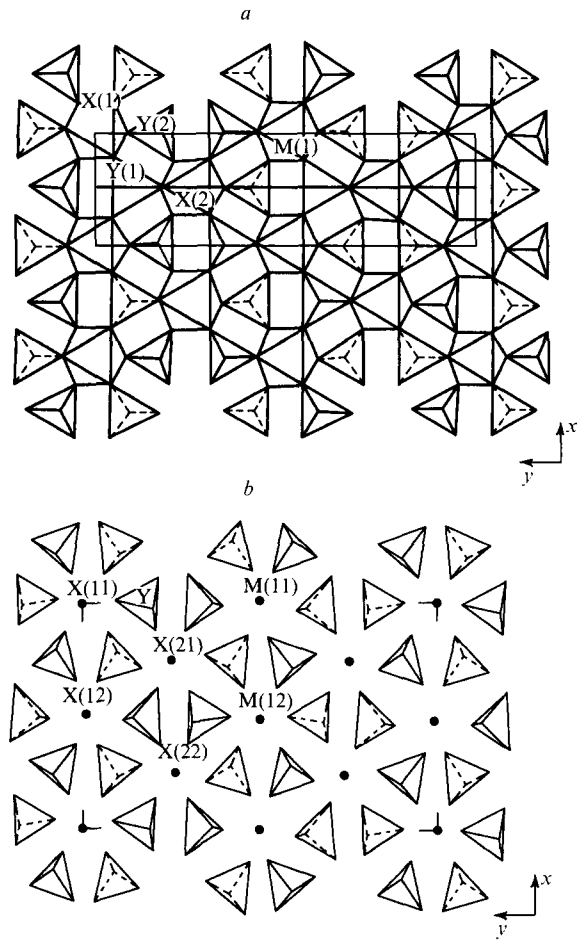


Figure 6. Projections of the bredigite structure on to the xy plane. Ideal (*a*) and real (*b*) arrangements.[44]

numbers of the sites are smaller than in the ideal structure. However, when account is taken of the longer distances, they correspond to the coordination numbers of the sites in the ideal structure.

It has been established that the bredigite structure occurs also for the solid solutions in the range $(Ca_{1.8}Mg_{0.2})SiO_4-(Ca_{1.7}Mg_{0.3})SiO_4$.[19,152] If the formulae of the compounds $(Ca_{1.8}Mg_{0.2})SiO_4$[19] and $(Ca_{1.7}Mg_{0.3})SiO_4$ (see Ref. 152) are adjusted to the composition reflecting the ideal crystal-chemical formula, they become $Ca_{7.2}Mg_{0.8}(SiO_4)_4$ and $Ca_{6.8}Mg_{1.2}(SiO_4)_4$. In the solid solutions between these phases, the $M^{[6]}$ site and one of the $Y^{[9]}$ sites are statistically occupied by magnesium and calcium cations. The remaining sites, $X^{[12]}$ and $Y^{[10]}$, are occupied by calcium cations only. The compound $Ca_7Mg(SiO_4)_4$ corresponds to the ideal formula of the bredigite structure (without a statistical occupation of the sites).

When account is taken of the dimensions of the X, Y, and M polyhedra, one may expect the formation of the compound $BaCa_6Mg(SiO_4)_4$, in which the cations occupy the following sites: $X^{[12]}$ by Ba^{2+}, $Y^{[10]}$ and $X^{[9]}$ by Ca^{2+}, and $M^{[6]}$ by Mg^{2+}. Apparently the ideal structure is not produced in this case. In order to obtain the ideal structure of the bredigite type, it is more likely to be useful to employ the compounds $K_3R(PO_4)_2$ (the compounds with R = Sc or Lu have the ideal glaserite structure)[5,6] and $KBaPO_4$ (with a structure of the β-K_2SO_4 type)[7] or $BaNaPO_4$ (glaserite structural type)[134] and $KBaPO_4$ (type β-K_2SO_4 structure).[17] In this case, one may expect the formation of the $Ba_2K_5R(PO_4)_4$ (R = Lu, Sc) and $Ba_4K_2Na_2(PO_4)_4$ phases respectively. In the latter compound,

the second sodium cation may occupy one of the Y sites together with Ba, as in the case of $BaNaPO_4$.[134]

The modelling of the phases based on the bredigite structure examined above is important for the synthesis of compounds with the required physicochemical properties. Firstly, the combination of two structures with different coordination polyhedra into one structure makes it possible to introduce various cations into a lattice of this kind. The problem of the synthesis of multifunctional materials is thus solved. Secondly, the successive alternation of polyhedra of different structures makes it possible to increase the distances between like cations, preventing thereby their interaction, which may improve the physicochemical characteristics of the materials. The latter is important in the synthesis of phosphors and diamagnetic materials with cations having magnetic properties.

4. The palmierite $K_2Pb(SO_4)_2$ structural type

In contrast to α-$Ca_3(PO_4)_2$ (β-K_2SO_4 structural type), the phosphates of divalent elements with large radii, namely $M_3(PO_4)_2$ (M = Sr, Ba, Pb),[26,153] $Pb_4(PO_4)_2CrO_4$,[154] and also the molybdate $K_2Pb(MoO_4)$[155] crystallise in the structural type corresponding to the natural mineral palmierite $K_2Pb(SO_4)_2$.[23] Barium and strontium vanadates and arsenates also belong to this structural type.[25-27]

In the $K_2Pb(SO_4)_2$ structure, the potassium cation occupies the YO_{10} decahedron, while the lead cation occupies the XO_{12} dodecahedron. The XO_{12} coordination polyhedron is formed by the edges of six tetrahedra (Fig. 3*a*). The X–O distances are divided into two types: six short distances (2.83–2.85 Å) form an appreciably extended (along the $\bar{3}$ axis) trigonal antiprism, while six long ones (3.4–3.5 Å to the apical oxygen atoms) are located in the equatorial plane of the antiprism. The symmetry of this polyhedron is $\bar{3}2/m$. XO_{12} is adjoined below and above (along the $\bar{3}$ axis) by two YO_{10} polyhedra (Fig. 7). They have triangular faces in common with the antiprism. The YO_{10} polyhedron is formed by three edges of three tetrahedra (equatorial plane), three oxygen atoms in three other tetrahedra (at distances of ~3 Å), and one (apical) oxygen atom on the threefold axis (Figs 3*b* and 7).

Overall, the palmierite structure is made up of $\ldots-YO_{10}-XO_{12}-YO_{10}-EO_4-EO_4-\ldots$ columns and its crystal-chemical formula is $X^{[12]}Y_2^{[10]}(EO_4)_2$. The Sr^{2+}, Ba^{2+}, and Pb^{3+} ions occupy the large XO_{12} and YO_{10} polyhedra.

At first sight, the existence of the double molybdates $M_5R(MoO_4)_4$ (M = K, Rb; R = rare earth, Bi, Y, Al, Fe), crystallising in the palmierite structural type, appears unusual. Such compounds have been found in the study of the $M_2MoO_4-R_2(MoO_4)_3$ systems.[28,29] It follows from crystal-chemical data that the X sites may be occupied also by small cations. To a first approximation, their coordination number is then six (the nearest six oxygen atoms). As a result of the ease of the rotation of the tetrahedra, coordination numbers different from those in the ideal structure may occur in the palmierite-like structure. For example, the phase transition in $Pb_3(PO_4)_2$ is accompanied by an increase in the symmetry from monoclinic to trigonal at 473 K.[154]

The mobility of the tetrahedra in the palmierite-like structure promotes the formation of coordination polyhedra characteristic of the given trivalent cation. For this reason, the compounds $M_5R(MoO_4)_4$ are formed for the entire series of lanthanide, bismuth, iron, and aluminum cations.[28-32,155-161] Analogous tungstates are formed only for M = K or Rb and R = Bi, La, or In.[162-165] An intrinsic distortion of the ideal palmierite structure, precisely characteristic of the given compound, occurs in each case (Table 3).

With the aid of the crystal-chemical formula $X^{[6+6]}Y_2^{[9+1]}(EO_4)_2$ and the characteristics of the environment of the X site, one may predict the compositions of the $M_5R(MoO_4)_4$ phases, bypassing the laborious investigation of phase diagrams. Taking into account the fact that palmierite-like structures include large and small cations or only large cations, one may expect that isovalent or heterovalent substitutions would entail the formation of the following phases: $M'_4NaR(MoO_4)_4$ (M' = K, Rb); $SrBa_2(PO_4)_2$; $BaSr_2(PO_4)_2$; $M'MR(PO_4)_2$ (M' = K, Rb; M = Sr, Ba; R = Ln, Y, Bi, Fe, Al); $M_2R(SiO_4)_2$ (M = Sr, Ba; R = Ce, Zr, Hf); $M_2RPO_4SiO_4$ (M = Sr, Ba; R = Ln, Fe, Al, Bi, Y); $M'MRPO_4SiO_4$ (M' = Sr, Ba; M = K, Rb; R = Ce, Zr, Hf). A series of compounds having similar compositions and structures had been synthesised earlier, for example, $Sr_4(PO_4)_2CrO_4$,[166] $Ba_3(TaO_4)_2$,[167] $M'_2M(EO_4)_2$

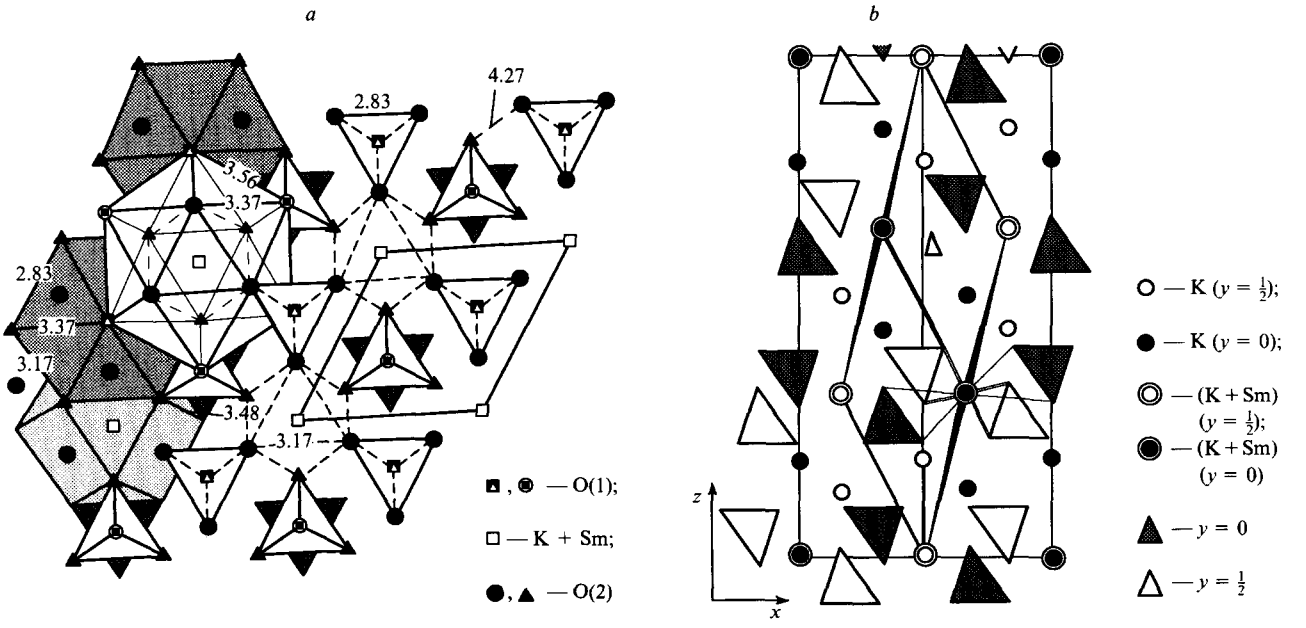


Figure 7. Projection of the structure of palmierite $K_5Sm(MoO_4)_4$ on to the *xy* plane: (*a*) $0.10 \leqslant z \leqslant 0.44$, (*b*) *xz*.[156]

Table 3. X-Ray diffraction characteristics of certain palmierite-like phases.

Compound	a/Å	b/Å	c/Å	Angle /°			Space group	Ref.
				α	β	γ		
$K_2Pb(SO_4)_2$[a]	5.50	5.50	20.863				$R\bar{3}m$	23
$K_2Pb(MoO_4)_2$[a]	10.38	7.81	11.98		115.9		$P2$	155
$Sr_3(PO_4)_2$[a]	5.621	5.621	20.14				$R\bar{3}m$	26
$Ba_3(PO_4)_2$[a]	5.783	5.783	21.34				$R\bar{3}m$	26
$Sr_3(VO_4)_2$	5.621	5.621	20.14				$R\bar{3}m$	27
$Ba_3(VO_4)_2$[a]	5.762	5.762	21.29				$R\bar{3}m$	27
$Sr_3(AsO_4)_2$	5.581	5.581	19.98				$R\bar{3}m$	27
$Ba_3(AsO_4)_2$	5.753	5.753	21.18				$R\bar{3}m$	27
α-$Pb_3(PO_4)_2$[a]	5.53	5.53	20.30				$R\bar{3}m$	154
β-$Pb_3(PO_4)_2$[a]	13.816	5.692	9.429		102.4		$C2c$	154
$K_5Nd(MoO_4)_4$[a]	10.360	17.943	14.301		103.98		$P2/m$	32
α-$K_5Y(MoO_4)_4$[a]	10.453	10.453	41.04				$R\bar{3}m$	157
β-$K_5Y(MoO_4)_4$	10.478	6.034	7.736		118.0		$C2/m$	159
α-$K_5In(MoO_4)_4$	10.30	18.21	14.99	90.97	106.61	89.58	$P1$	158
β-$K_5In(MoO_4)_4$[a]	10.46	12.092	14.625		114.0		Aa	158
$K_5Bi(MoO_4)_4$[a]	6.019	6.019	41.761				$P\bar{3}1m$	32
$Rb_5Gd(MoO_4)_4$[a]	10.604	18.349	14.725	90.11	104.41	89.99	$P1$	32
α-$Rb_5Al(MoO_4)_4$[a]	10.520	6.078	8.470		114.5		Cc	161
β-$Rb_5Er(MoO_4)_4$	11.44	7.99	11.19		113.0		$P2/c$	160
$K_5Sm(MoO_4)_4$[a]	5.978	5.978	20.79				$R\bar{3}m$	156

[a] The crystal structure has been determined.

(E = S, Cr),[168-170] $K_5R(SO_4)_4$ (R = Ln),[171] $M_8Th(MoO_4)_6$,[172] and $K_3(MoO_4)(ReO_4)$.[173]

In the case of both palmierite and other structural types, an important factor in the prediction of such phases is the estimation of their crystal lattice energies. An estimate of this kind can be achieved provided that the coordinates and the 'effective' charges of the atoms are known.

5. The NASICON structural type

The NASICON structural type occurs for cations with small radii (Sc^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Zr^{4+}, Ti^{4+}, Nb^{4+}, Nb^{5+}) accommodated in the (RO_6) octahedra. A three-dimensional skeletal composition made up of RO_6 octahedra, sharing their vertices with the EO_4 tetrahedra, is characteristic of structures of this class (Fig. 8). A framework of this kind was first described by Abrahams and Bernstein.[174] Subsequently, as the structures of other representatives of this family were determined, the characteristic features of its structure were refined.[33-41,62,68-73,95] At present, there are more than 400 publications on the structures and properties of compounds of this class. Many of them are devoted to the elucidation of the mechanism of ionic conduction on the basis of crystal-chemical data.

The formula $M_nR_2(EO_4)_3$, where $0 \leqslant n \leqslant 4$, describes all the possible compounds with the NASICON structure.[41] The NASICON-like phases are based on the three-dimensional framework $\{[R_2(EO_4)_3]^{p-}\}_{3\infty}$ where E = P, Si, S, Mo, As, W, Se, or Ge. The sodium cation is usually employed as the vacancy-filling cation (M), but it can be replaced by Li^+ and Cu^+ or by Cu^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}.

The structural framework is threaded by channels of two types, *I* and *II*, along the *c* axis of the unit cell (Fig. 8). The zigzag network of type *III* channels passes at right angles to them along the [010] direction. Channels *III* intersect channels *I* and *II*, forming a three-dimensional cavity framework. The channels have variable widths, the cross-sections of the narrowest sites being 1.0 Å for type *I* channels, 1.1 Å for type *II* channels, and 0.9 Å for type *III* channels. Cations with radii of 1.2–1.4 Å can be placed in the wide spaces within the channels (at the intersection of channels *I* with channels *III* and of channels *II* with channels *III*). In the above cavities, it was possible to differentiate two sites — M(1) and M(2) (Fig. 9).

If the space group $R\bar{3}c$ is adopted as the basis (the highest symmetry for the compounds under discussion), then in this case the sixfold M(1) site is an extended antiprism with distances of ~2.6 Å to the nearest six oxygen atoms (the other six oxygen atoms are separated by long distances of ~3.7 Å). The eightfold M(2) site is surrounded by eight oxygen atoms at distances of ~2.47–2.89 Å and two oxygen atoms at distances of ~3.25 Å.

It follows from the analysis of the cross-sections of the channels that a cation with a radius of ~1 Å (for example, Na) can migrate through them. During the migration of sodium cations from the M(1) site to the M(2) site, the narrowest places are at the A–B–C and A–B–D faces (Fig. 9*b*).[175] When account is taken of the thermal displacements of the oxygen

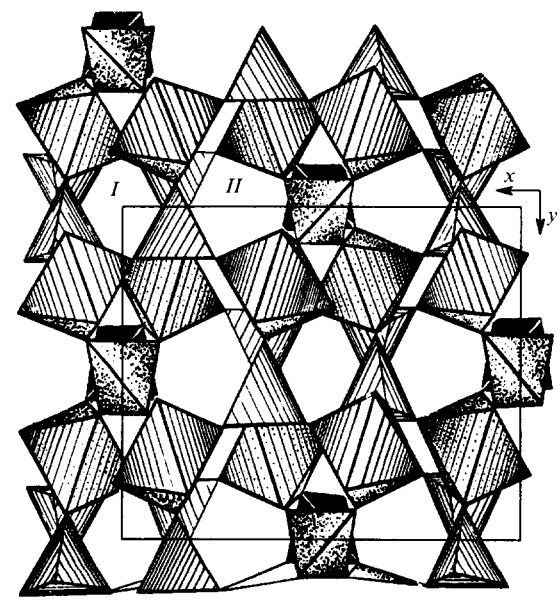


Figure 8. The framework of the $Sc_2(MoO_4)_3$ structure.[41]

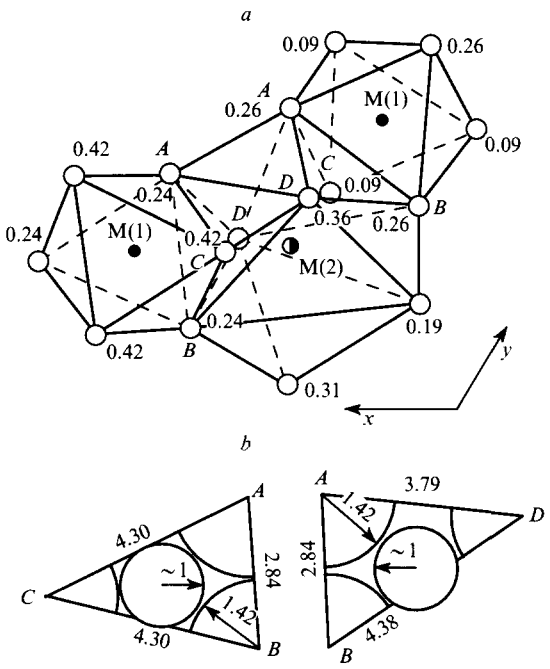


Figure 9. The NASICON structural type: (*a*) surroundings of the M(1) and M(2) sites; (*b*) the free space bounded by the common faces of the $M(1)O_6$ and $M(2)O_8$ polyhedra in the α-$Na_3Sc_2(PO_4)_3$ structure.[175]

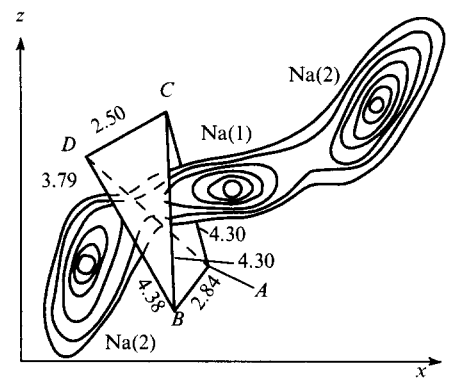


Figure 10. Distribution of the electron density of the sodium atoms in the conduction channels of the α-$Na_3Sc_2(PO_4)_3$ structure (60 °C).[67]

atoms, particularly with increase in temperature, the sodium cations (r_{VI} = 1.02 Å) can migrate from one site to the other without any obstacles. This fact is indeed the reason for the appearance of superionic conduction in compounds of this class.[33,38,65,66] The mobility of sodium cations has been confirmed experimentally by the distribution of their electron density within the conduction channels observed even at 60 °C in α-$Na_3Sc_2(PO_4)_3$ (Fig. 10).[67]

It follows from the analysis of the number of polyhedra and their surroundings that the crystal-chemical formula of the NASICON structural type is $M(1)^{[6]}M(2)_3^{[8]}R_2^{[6]}(EO_4)_3$. A necessary condition for the occurrence of the structural type under discussion is the small size (<0.8 Å) of the cations R. Their valence should be in the range $2 \leqslant p \leqslant 5$. Phases with valences of 2 and 5 have not been described in the literature. However, phases with 'formal' valences of 2.5 (2R = $Cr^{3+} + Mg^{2+}$)[37] and 4.5 (2R = $Nb^{5+} + Ti^{4+}$)[34] are known. The additional atoms M can be accommodated at the M(1) and M(2) sites. Structures with fully occupied M(1) and M(2) sites [$Na_4Zr_2(EO_4)_3$ (E = Si, Ge);[39,40] $Na_{4.5}R_{1.5}(PO_4)_3$ or $Na_3R(PO_4)_2$ (R = Tm, Yb, Lu)[148]], structures in which only the M(1) sites are occupied [$NaR_2(PO_4)_3$, R = Ti, Zr)[62,73]], structures in which only the M(2) sites are occupied (jointly with the vacancies) [$Cu^{I}Ti_2(PO_4)_3$ (see Ref. 95) and the low-temperature $Na_3Sc_2(PO_4)_3$ (see Ref. 68)], structures with a statistical occupation of the M(1) and M(2) sites (jointly with the vacancies) [the high-temperature $Na_3Sc_2(PO_4)_3$ (see Ref. 67)], and structures with fully vacant M(1) and M(2) sites [$R_2(EO_4)_3$ (R = Sc, Fe; E = Mo, S),[41,176,178] $MM'(PO_4)_3$ (M = Mo, Nb; M' = Ti, Zr),[179] and $NbTi(PO_4)_3$ (see Ref. 34)] have been found.

Depending on the set of cations, the ideal trigonal unit cell may be distorted to an orthorhombic or monoclinic cell. Examples of certain compounds of the structural type under consideration are presented in Table 4. As can be seen from the Table 4, different distortions of the unit cell occur even for a set of the same cations. The symmetry of the cell is appreciably influenced by the distribution of the cations among the structural sites. A highly symmetrical cell is characteristic of compounds with an occupied M(1) site. In this case, an appreciable cationic conductivity occurs at a temperature above 500 K. When the M(2) site is fully occupied, the cationic conductivity even appears at room temperature.[62]

Table 4. X-Ray diffraction characteristics of certain NASICON-like phases.

Compound	*a*/Å	*b*/Å	*c*/Å	β/°	Space group	Ref.
$Sc_2(MoO_4)_3$[a]	13.242	9.544	9.637		*Pbcn*	41
m-$Fe_2(SO_4)_3$[a]	8.29	8.53	11.63	90.8	$P2_1/n$	177
$Fe_2(MoO_4)_3$[a]	15.7	9.23	18.2	125.3	$P2_1/n$	176
$NaZr_2(PO_4)_3$[a]	8.80	8.80	22.76		$R\bar{3}c$	73
$KZr_2(PO_4)_3$	8.71	8.71	23.89		$R\bar{3}c$	181
$RbZr_2(PO_4)_3$	8.66	8.66	24.38		$R\bar{3}c$	181
$CsZr_2(PO_4)_3$	8.62	8.62	24.86		$R\bar{3}c$	181
$Na_3Zr_2Si_2PO_{12}$[a]	15.128	8.722	8.793	125.76	$C2/c$	62
β-$Na_3Sc_2(PO_4)_3$[a]	16.10	9.11	8.93	127.2	*Bb*	68
α-$Na_3Sc_2(PO_4)_3$[a]	8.927	8.927	22.34		$R\bar{3}c$	67
$Na_4Zr_2(SiO_4)_3$[a]	9.10	9.10	22.07		$R\bar{3}c$	39
$Na_4Zr_2(GeO_4)_3$[a]	9.429	9.429	22.53		$R\bar{3}c$	40
$CuTi_2(PO_4)_3$[a]	8.523	8.523	21.303		$R\bar{3}c$	95
$Cu_{0.5}Ti_2(PO_4)_3$	8.84	8.84	22.77		$R\bar{3}c$	82
$H_{0.5}Cu_{0.5}Zr_2(PO_4)_3$	8.84	8.84	22.75		$R\bar{3}c$	96
$HZr_2(PO_4)_3$	8.80	8.80	23.23		$R\bar{3}c$	180

[a] The crystal structure has been determined.

Detailed information about the structure of compounds of the NASICON type made it possible to synthesise, with the aid of isovalent and heterovalent substitutions in the cationic and anionic sublattices, new superionic materials with low temperatures of the onset of ionic conduction, for example, $Na_{3+x}Cr_{2-y}Mg_z(PO_4)_3$,[37] $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$,[62] $NbTi(PO_4)_3$,[34] $Na_{1+x}Zr_{2-x}In_x(PO_4)_3$,[72] $HZr_2(PO_4)_3$,[180] $Cu^{II}_{0.5}Ti_2(PO_4)_3$,[82] $Na_{2x}M_{2x}Sc_{2-2x}(MoO_4)_3$ (M = Zn, Cd, Mg),[90] $Cu^{I}Zr_2(PO_4)_3$,[93] $H_{0.5}Cu^{I}_{0.5}Zr_2(PO_4)_3$,[96] and many others.

It follows from the data presented above that the NASICON structural type is based on the $\{[R_2(EO_4)_3]^{p-}\}_{3\infty}$ three-dimensional framework. Other atoms can be introduced into such a framework by means of substitution or insertion with formation of new phases. A framework of a similar kind has been encountered also in compounds of other classes belonging to the garnet $Ca_3Zr_2(Si,AlO_{12})$[42] and langbeinite $K_2Mg_2(SO_4)_3$ (see Ref. 182) structural types. The crystal-chemical analysis of the $\{[R_2(EO_4)_3]^{p-}\}_{3\infty}$ framework for these structural types has been described in detail.[183]

6. The whitlockite structural type

The low-temperature β-modification of calcium orthophosphate is isostructural with the natural mineral whitlockite ($R3c$, $Z = 3$) $Ca_{18.19}Mg_{1.17}Fe_{0.83}H_{1.62}(PO_4)_{14}$.[46] Projections of this β-$Ca_3(PO_4)_2$ structure with the highest information content are presented in Fig. 11. This structure is made up of isolated EO_4^{n-} tetrahedra, which bind the MO_n polyhedra into a three-dimensional framework via common vertices. Along the c axis in the structure, it is possible to differentiate two types of columns — A and B. In the type B column, the MO_8 polyhedra, containing calcium cations at the M(1), M(2), and M(3) sites and two tetrahedra alternate consecutively [M(1)O_8–M(3)O_8–M(2)O_8–PO_4–PO_4–...]. The type A column (along the 3 axis) consists of a sequence of polyhedra and cavities ...–PO_4–M(4)O_{15}–M(5)O_6–M(6)O_{10}–... (Fig. 12). The M(4) site in this column is vacant or partly occupied, while the M(6) site is always vacant.

The unit cell of β-$Ca_3(PO_4)_2$ contains 21 formula units.[99] In conformity with the stoichiometric formula of the compound, there are $63Ca^{2+}$ cations and $42PO_4^{3-}$ tetrahedra per unit cell. The $R3c$ symmetry presupposes the occupation of 66 sites (three 18-fold and two sixfold) by calcium cations. Consequently three cationic vacancies (□) are present in the unit cell.

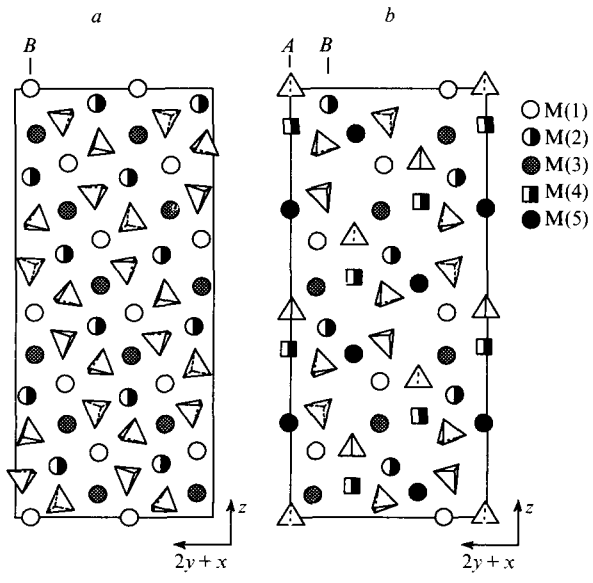


Figure 11. The layers in the β-$Ca_3(PO_4)_2$ structure: (*a*) layer with type *B* columns ($y = -0.25$); (*b*) layer with type *A* and *B* columns ($y = 0$).[103]

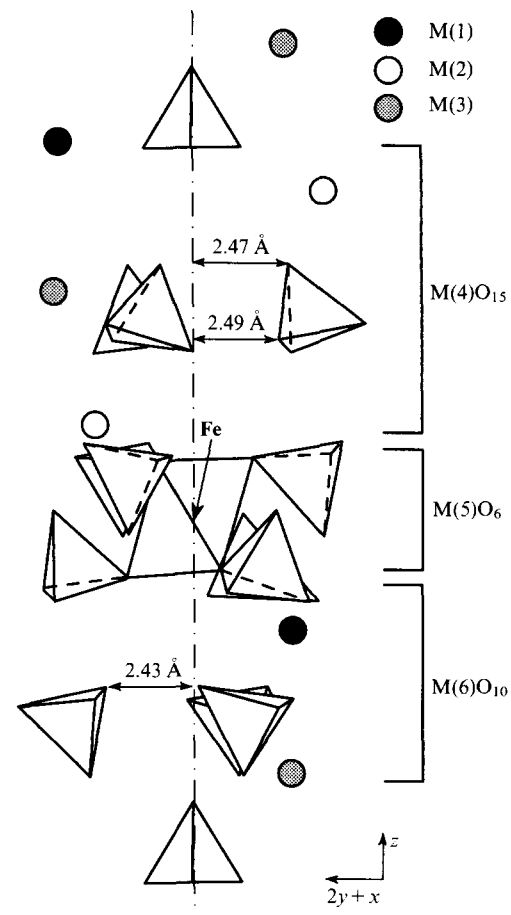


Figure 12. Fragment of a type *B* column in the $Ca_9Fe(PO_4)_7$ structure. Certain interatomic distances are indicated.[109]

The composition of the unit cell is reflected by the formula $Ca_3□_3(PO_4)_{42}$ ($Z = 1$) and its crystal-chemical analogue $Ca(1)^{[8]}_{18}Ca(2)^{[8]}_{18}Ca(3)^{[8]}_{18}Ca(4)^{[9]}_{3}□(4)^{[9]}_{3}Ca(5)^{[6]}_{6}(PO_4)_{42}$ where □ is a vacancy at the M(4) site. Having differentiated the calcium atoms with similar environments at the 18-fold M(1), M(2), and M(3) sites, we obtain the formula $Ca_{54}Ca_6Ca_3□_3(PO_4)_{42}$ ($Z = 1$) or, in an abbreviated form $Ca_9CaCa_{0.5}□_{0.5}(PO_4)_7$ ($Z = 6$).

The M(4) site is half-filled by calcium cations in β-$Ca_3(PO_4)_2$.[99] It is not structure-forming and theoretically may be both entirely free (6□) or fully occupied (6M). The boundary conditions (number of vacancies) make it possible to model phases with specified compositions.

The postulated compositions of the new compounds have been calculated taking into account the heterovalent substitutions of the Ca^{2+} cations by M^+, R^{3+}, and R^{4+}.[100–106, 108, 110] Different substitution schemes with formation or population of vacancies were used for the modelling of the compositions of the compounds:

(1) $9Ca^{2+} + 3□ = 6R^{3+} + 6□$, $Ca_3(PO_4)_2$–RPO_4 section, limiting composition $Ca_9R□(PO_4)_7$ ($Z = 6$);[100–103, 108]

(2) $3Ca^{2+} + 3□ = 6M^+$, $Ca_3(PO_4)_2$–M_3PO_4 section, limiting composition $Ca_{10}M(PO_4)_7$ (M = Si, Na, K,[104] Cu[105]) ($Z = 6$); (3) $9Ca^{2+} + 3□ = 6Mg^{2+} + 6M^+$, limiting composition $Ca_9MgM(PO_4)_7$ (M = Li, Na, K) ($Z = 6$);[106]

(4) $9Ca^{2+} + 3□ = 3R^{3+} + 9Na^+$, $Ca_3(PO_4)_2$–$Na_3R(PO_4)_2$ section, limiting composition $C_{18}Na_3R(PO_4)_{14}$ ($Z = 3$);[107, 184, 185]

(5) $6Ca^{2+} + 3□ = 3R^{4+} + 6□$, $Ca_3(PO_4)_2$–$R_3(PO_4)_4$ section, limiting composition $Ca_{19}R□_2(PO_4)_{14}$ (R = Ce) ($Z = 3$).[108]

Variable-composition phases with whitlockite-like structures are formed between $Ca_3(PO_4)_2$ and the limiting compositions.[101,103,104,107,108,160,161] This predetermines the existence of phases within the $Ca_3(PO_4)_2-Ca_{10}Na(PO_4)_7-Ca_{18}Na_3R.(PO_4)_{14}-Ca_9R\square(PO_4)_7$ tetragon.[107]

It follows from the analysis of the interatomic distances in the polyhedra of the whitlockite-type structure that the lanthanide elements should occupy the M(1)–M(3) sites, whilst the cations with $r<0.8$ Å should occupy the octahedral M(5) site.[110] There is sufficient space within the $M(4)O_{15}$ cavity to accommodate cations with a radius of ~1.5 Å (Na, K) but not enough to accommodate rubidium and caesium cations (Fig. 12). The Na and K cations can occupy different sites along the threefold axis in the $M(4)O_{15}$ cavity which are restricted by the distances to the O(12) and O(33) oxygen atoms.

The choice of the most suitable distribution of cations among the structural sites in the model compounds has been made taking into account the calculated Madelung constants.[186] Trivalent and tetravalent cations are most probably accommodated at the M(1) and M(2) sites, while monovalent cations are at the M(4) sites. Subsequent studies on the structures of $Ca_{10}Na(PO_4)_7$,[104] $Ca_9Fe(PO_4)_7$,[109]† and $Ca_9Eu(PO_4)_7$ (see Refs 188, 189) confirmed these calculations.

It is noteworthy that, in contrast to the glaserite, palmierite, β-K_2SO_4, and NASICON structural types examined above, the whitlockite-like crystal structure is not distorted after the insertion or substitution of cations in it (Table 5). The architecture of the whitlockite-type structure remains unchanged after the introduction into the lattice of cations having different dimensions and oxidation states. The stability of this structure predetermines the occurrence of reversible redox reactions without the destruction of the structure.[108–110]

Together with substitutions in the cationic lattice of a whitlockite-like structure, one can achieve substitution also in the anionic component, for example in accordance with the scheme

$$PO_4^{3-} + Ca^{2+} = SiO_4^{4-} + R^{3+}$$

with retention of the number of vacancies, or in accordance with the scheme

$$PO_4^{3-} + Ca^{2+} + 2\square = SiO_4^{4-} + 3M^{+}$$

with occupation of the vacancies in the structure. For trivalent cations with $r<0.8$ Å, the formula describing the limiting composition with six cations at the M(5) site is $Ca_{19}R_2(PO_4)_{12}(SiO_4)_2$, whilst for cations with $r>0.8$ Å the formula is $Ca_7R_4(SiO_4)_{14}$; intermediate compounds have the compositions $Ca_{15}R_6(PO_4)_8(SiO_4)_6$ and $Ca_9R_{12}(PO_4)_2(SiO_4)_{12}$ with full occupation of one or two 18-fold sites by the cations of the trivalent element. The limiting composition of compounds with a small trivalent cation (R′) at the M(5) site and a large cation (R) at the M(1)–M(3) sites is described by the formula $Ca_4R'_2R_{14}(SiO_4)_{14}$. In this case, when the M(5) site is occupied by the Mg^{2+} cation, the limiting composition is $Ca_5Mg_2R_{14}(SiO_4)_{14}$. The possibility of the existence of silicates and silicophosphates with a whitlockite-type structure is confirmed indirectly by the mineral cerite (Ce, La, Nd, Ca)$_9$(Fe, Mg, Al)$(SiO_4)_6(SiO_3OH)(OH)_3$,[187] which is isostructural with whitlockite.

Thus the data on the whitlockite structural type made it possible to calculate theoretically for the first time a wide range corresponding to the existence of variable-composition phases in the $Ca_3(PO_4)_2-Na_3PO_4-RPO_4$ ternary system[107] and the compositions of the individual compounds. This region is located within the $Ca_3(PO_4)_2-Ca_{10}Na(PO_4)_7-Ca_{18}Na_3R.(PO_4)_{14}-Ca_9R\square(PO_4)_7$ tetragon.

† The full structural data have been published by B I Lazoryak, V A Morozov, A A Belik, S S Krasnov, V Sh Shekhtman. *J.Solid State Chem.*, **121**, 1(1966).

Table 5. X-Ray diffraction characteristics of certain whitlockite-like phases (space group *R3c*).

Compound	*a*/Å	*c*/Å	Ref.
$Ca_{18.19}(Mg_{1.17}Fe_{0.83})H_{1.62}(PO_4)_{14}$ [a]	10.330	37.103	46
β-$Ca_3(PO_4)_2$ [a]	10.439	37.375	99
$Ca_3(AsO_4)_2$ [a]	10.77	37.81	190
$Ca_3(VO_4)_2$ [a]	10.809	38.028	191
$Ca_{18}Mg_2H_2(PO_4)_{14}$ [a]	10.350	37.085	192
$Ca_{18}Mn_2H_2(PO_4)_{14}$ [a]	10.438	37.15	193
$Ca_{20.23}Mg_{0.77}(PO_4)_{14}$ [a]	10.401	37.316	194
$Ca_{18.97}Mg_{2.03}(PO_4)_{14}$ [a]	10.337	37.068	194
(Ce,La,Nd,Ca)$_9$(Fe^{III},Mg,Al) × × $(SiO_4)_6(SiO_3OH)(OH)_3$	10.779	38.061	187
$Ca_9Fe(PO_4)_7$ [a]	10.3391	37.130	109
$Ca_9FeH_{0.9}(PO_4)_7$ [a]	10.354	37.165	109
$Ca_9La(PO_4)_7$	10.492	38.55	101
$Ca_{10}Cu(PO_4)_7$	10.442	37.39	105
$Ca_{10}Li(PO_4)_7$	10.421	37.38	104
$Ca_{10}Na(PO_4)_7$	10.442	37.31	104
$Ca_{10}K(PO_4)_7$	10.471	37.29	104
$Ca_9MgLi(PO_4)_7$	10.321	37.06	106
$Ca_9MgNa(PO_4)_7$	10.346	37.04	106
$Ca_9MgK(PO_4)_7$	10.398	36.96	106
$Ca_{18}Na_3Fe(PO_4)_{14}$	10.373	37.18	107
$Ca_{18}Na_3Nd(PO_4)_{14}$	10.458	37.39	107
$Ca_{19}Cu_2(PO_4)_{14}$	10.3638	37.219	110
$Ca_{19}Cu_2H_2(PO_4)_{14}$	10.3982	37.298	110

[a] The crystal structure has been determined

IV. The structures and physicochemical properties of the materials

In the search for new or improved known materials with specified properties, synthetic chemists must either estimate theoretically or postulate the properties which the newly formed compounds will have. Known prototypes are most often used for such purposes and more rarely, data on the structure of the solid material. Certain possibilities for the prediction of properties on the basis of crystal-chemical data will be considered in this section. We shall deal with certain approaches to the solution of problems of this kind.

Since the 1960s, a vigorous search for laser materials and phosphors has been prosecuted. Some of them have found applications in engineering. One of the most important characteristics of such materials is the lifetime (τ) of the excited state and the quantum yield. These two characteristics are interrelated. An increase in the concentration of the activator in the matrix is usually accompanied by a decrease in the lifetime and an increase in the quantum yield. According to the data of Hong and Chinn,[7] the optimum ratio of these parameters is observed for materials containing isolated NdO_x polyhedra, which prevent the Nd–Nd interaction and hence the concentration-induced quenching, and in which the polyhedron surrounding Nd^{3+} has no centre of inversion, since the intensity of the emission is largely associated with electric dipole transitions.

In laser materials with a high Nd^{3+} concentration ($>10^{21}$ cm^{-3}, when the condition of 'localness' does not hold),[195] the $Nd^{3+}-Nd^{3+}$ distances are 4.65–6.66 Å. As can be seen from the data presented in Table 6, the lifetime of the metastable levels for isostructural compounds, for example for $M_5B(MoO_4)_4$, increases with increasing $Nd^{3+}-Nd^{3+}$ distance. However, such a dependence cannot be traced for the entire series of compounds presented in Table 6 because the symmetry of the surroundings of the activator ion changes in these phases. Thus the $Nd^{3+}-Nd^{3+}$ distances in the $K_3Nd(PO_4)_2$ (see Ref. 7) and $Na_3Nd(PO_4)_2$ (see Ref. 13) structures, based on β-K_2SO_4,

Table 6. The lifetimes of the excited state (τ) and the Nd – Nd distances in certain laser materials.

Compound	d_{Nd-Nd}/Å	τ/μs [a]		Ref.
		max	min	
NdP_5O_{14}	5.194	115	320	196
$KNdP_4O_{12}$	6.661	100	275	197
$LiNdP_4O_{12}$	5.62	135	325	198
$Na_5Nd(WO_4)_4$	6.45	85	220	196
$K_5Nd(MoO_4)_4$	5.98	70	290	199
$Rb_5Nd(MoO_4)_4$	6.08	79	350	199
$K_3Nd(PO_4)_2$	4.873	21	460	7
$Al_3Nd(BO_3)_4$	5.917	19	50	200
$Na_3Nd(PO_4)_2$	4.65	see [b]	see [b]	13

[a] The values τ for the maximum (max) and minimum (min) Nd^{3+} concentrations are quoted; [b] the lifetime of the metastable level has not been quoted [13] for $Na_3Nd(PO_4)_2$.

differ little (Table 6) and the lifetime of the metastable $Na_3Nd(PO_4)_2$ level is probably the same as for $K_3Nd(PO_4)_2$.

Crystal-chemical analysis makes it possible to estimate the laser characteristics of the compounds postulated. The structural type of bredigite, the structure of which contains fragments of the glaserite and β-K_2SO_4 structural types, should be promising in this connection. The insertion of glaserite columns between type β-K_2SO_4 columns would increase the $Nd^{3+}-Nd^{3+}$ distance by a factor of 2 and the latter, would amount to 9 Å on average. The neodymium concentration would diminish by a factor of 2 and would be 2×10^{21} cm^{-3} [in $N_3Nd(PO_4)_2$, the Nd^{3+} concentration is 4×10^{21} cm^{-3}]. In the postulated compound $M_3Na_3NdR(PO_4)_4$ (M = K, Rb; R = Lu, Sc), the minimum distance between the Nd atoms (5.4 Å) may be achieved only in the C column (Fig. 1). The lifetime of this compound would be ~100 μs, as for NdP_5O_{14}.[196] This conclusion is based on the fact that, as in NdP_5O_{14}, the two neighbouring Nd polyhedra in $M_3Na_3NdR(PO_4)_4$ do not have a common tetrahedron linking them and are separated by two tetrahedra or the NaO_x polyhedron.

The lifetimes of glaserite-like phases containing neodymium atoms may be estimated similarly. For example, the compound $K_2NaNd(PO_4)_2$ [obtainable by the heterovalent substitution $K^+ + 2SO_4^{2-} = Nd^{3+} + 2PO_4^{3-}$ in $K_3Na(SO_4)_2$] may serve as a laser material. Regardless of which of the polyhedra ($X^{[6+6]}$ or $Y^{[4+6]}$) is occupied by Nd^{3+} cations, the minimum $Nd^{3+}-Nd^{3+}$ distances in the postulated phase would be determined by the X – X or Y – Y distances. These distances are the same and amount to 5.68 Å in glaserite itself. Two neighbouring (X or Y) polyhedra in $K_2NaNd(PO_4)_2$ are linked together by an edge of the tetrahedron, as in $M_5Nd(MoO_4)_4$. These data suggest that the lifetime of the metastable level in the compound $K_2NaNd(PO_4)_2$ would be of the same order of magnitude as in $M_5Nd(MoO_4)_4$. It follows from the data presented that, by using crystal-chemical ideas, it is possible to estimate to a first approximation the characteristics of laser materials.

In optical materials, the luminescence (lasing) line width depends on the number of activator cations, their surroundings, and the quality of the crystals. The smaller the difference between the surroundings of the activator cations, the smaller the half-width of the emission lines. Despite this, dilution is used to diminish the concentration-induced quenching in laser materials. For this purpose, Nd^{3+} cations are substituted by La^{3+}, Lu^{3+}, Y^{3+}, or Bi^{3+} cations. The correct choice of the diluent cation can be achieved only by taking into account crystal-chemical data. For example, in order to reduce the concentration-induced quenching in $M_5Nd(MoO_4)_4$, it is more promising to substitute Nd^{3+} by La^{3+} and not by Y^{3+}, Lu^{3+}, or Bi^{3+}, which have surroundings in the palmierite-like matrix different from those of Nd^{3+}.[31]

The luminescence line width of the lanthanide cation in $M_5R(MoO_4)_4$ (R = rare earth) is appreciably increased owing to the presence of several RO_x polyhedra in close proximity.[32] When a second trivalent element (diluent) is introduced into such a material, the line width increases appreciably, which impairs the optical characteristics of the material. A similar effect is observed also in the $Na_3Nd_{1-x}R_x(PO_4)_2$ (R^{3+} = Gd, Lu, Y) solid solutions. The surroundings of Nd^{3+} and R^{3+} in these phases are different.[16]

Apart from crystal-chemical data, in selecting diluent cations it is useful to employ in certain cases other structure-sensitive methods, for example optical data may be employed. This extremely sensitive method makes it possible to determine the number of active centres and the limits of existence of the phases of two structurally similar compounds. In certain cases this method is the only one suitable for the elucidation of the regions of homogeneity. For example, in the study of the solid solutions in the $Na_3Eu(PO_4)_2-K_3Eu(PO_4)_2$, $Na_3Gd(PO_4)_2-R_3Gd(PO_4)_2$,[201] $NaCaPO_4-Na_3Eu(PO_4)_2$, $NaSrPO_4-Na_3Eu(PO_4)_2$,[142] and $Ca_3(PO_4)_2-Na_3R(PO_4)_2$ (R = Nd, Eu, Er) solid solutions,[185] only the luminescence method made it possible to discover the limits of existence of the solid solutions. The X-ray powder diffraction analysis of a mixture of compounds with similar structures entails a large error in this case or altogether fails to distinguish them.

It has been established that the number of nonequivalent Eu^{3+} sites in the $Na_3Eu(PO_4)_2-K_3Eu(PO_4)$ solid solutions[201] is the same as in the corresponding initial compounds. There are six such nonequivalent sites in $Na_3Eu(PO_4)_2$ and one in $E_3Eu(PO_4)_2$ (Fig. 13). It follows from the experimental determinations of the regions of homogeneity[142,185,201] that the substitution of cations in the crystal lattice is accompanied by slight changes in the surroundings of the R^{3+} ions, which cannot be predicted solely on the basis of crystal-chemical data or be determined by X-ray diffraction.

Analysis of the geometry of the polyhedra and of their relative positions in the β-K_2SO_4 and glaserite structures made it possible to postulate initially the composition and then also to synthesise effective phosphors with lanthanide elements[141,202–206] characterised by a long lifetime and a high luminescence intensity. In the search for such materials, various structural types were considered and the compositions of the compounds were modelled within the framework of a single structural type. For example, the introduction of Ce^{3+} and Tb^{3+} cations into a type β-K_2SO_4 matrix increased the quantum yield as a result of energy transfer from Ce^{3+} to Tb^{3+}.[203–205]

The ability of the tetrahedra to rotate readily, noted in the β-K_2SO_4 structural type, and the occurrence of low-temperature phase transitions in compounds of this type have been used by Elouadi et al.[207] to predict the possible ferroelectric and piezoelectric transitions in the compounds $MM'PO_4$ ($M = Na^+$, K^+; $M' = Ca^{2+}$, Zn^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}). It has been established experimentally that such transitions occur in the temperature range 585 – 1470 K.[207]

In a study of the structure of the low-temperature modification of $Na_3Sc_2(PO_4)_3$, it has been found[68] that sodium occupies two close sites in the M(2) polyhedron with an 'effective' distance of 1.28 Å. The occupations of these sites differ by a factor of 1.7. Such non equivalence of the site occupations in the M(2) polyhedron is equivalent to the existence in the structure of a system of uncompensated dipoles,[68] the presence of which suggests ferroelectric properties [it has been established experimentally[66] that α-$Na_3Sc_2(PO_4)_3$ is a ferroelectric substance up to 333 K].

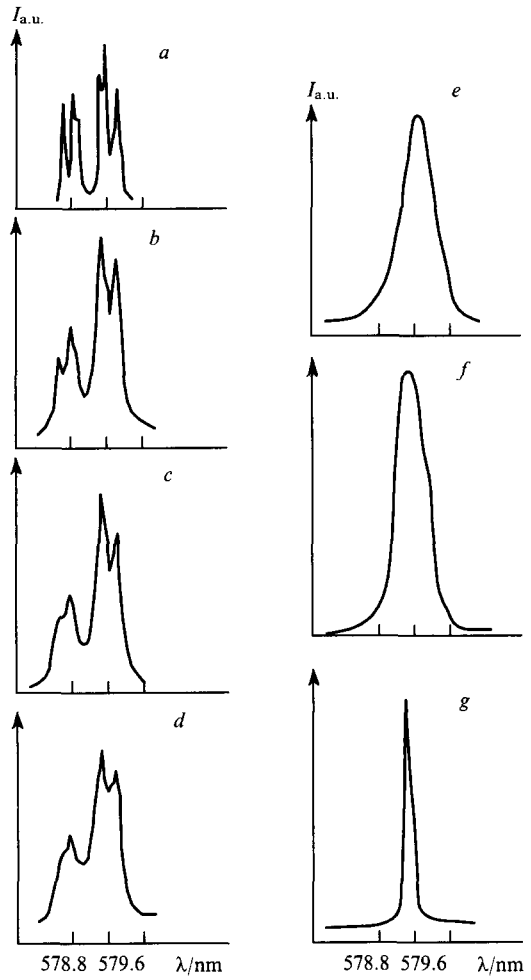


Figure 13. Luminescence spectra of Eu^{3+} in the region of the transition $^5D_0 \rightarrow {}^7F_0$ in $Na_{3-x}K_xEu(PO_4)_2$: (*a*) $x = 0$; (*b*) $x = 0.15$; (*c*) $x = 0.4$; (*d*) $x = 0.6$; (*e*) $x = 1$; (*f*) $x = 1.5$; (*g*) $x = 3$.[201]

V. Conclusion

It follows from the data presented in this review that crystal chemistry constitutes an effective instrument for the modelling of the compositions of new compounds with a specified structure, for the prediction of new materials with specified properties, for the modification and improvement of the properties of materials, and for the correct interpretation of experimental data concerning the regions of existence of the initial phases and their polymorphic transitions.

Furthermore, reliable information about the structure of a solid makes it possible to estimate the crystal lattice energies of known and model phases, to establish the symmetry and the coordination environment of the cations in the compounds, to determine the geometrical characteristics of the polyhedra in the structure and their relative positions, to determine or estimate the cation–cation and cation–anion distances in the model phases, to introduce chemical elements with different dimensions and oxidation states into the crystal lattice of the structure in order to obtain materials with the required properties, and to deform the structure in order to improve the properties or obtain materials with unusual properties (for example, oxide superconductors).

However, at the present time crystal-chemical data are used effectively only for the interpretation of experimental data and to only a very slight extent (excluding the search for superconducting materials) for the prediction of the compositions of materials and their properties. The reason for this is the lack of a well-founded algorithm for the application of the crystal-chemical data accumulated hitherto (due to the fact that the relevant studies have been shared between synthetic and structural chemists).

At the present time, problems in materials science are mainly considered from the composition–structure–property standpoint. Such a scheme includes the following components: (1) empirical search for the compound; (2) the study of its structure; (3) the study of its properties. On the other hand, the structure–property–composition scheme proposed in the present review includes the following components: (1) analysis of the structures of the compounds or classes of compounds; (2) prediction of the possible properties; (3) prediction of the compositions of the compounds with the necessary properties; (4) synthesis of the predicted compounds; (5) test of the properties; (6) refinement of the structure (if necessary). At the present level of development of solid state chemistry and information science, this approach is quite realistic. It makes it possible to shorten the time required to search for the necessary compositions of the compounds or phases and also to reduce the extent to which the equipment is used and to diminish the expenditure on the search stages. The structures of a large number of inorganic compounds have now been established; there exists a data bank for the structures of many inorganic phases; the radii of the cations in fluoride and oxide phases have been determined fairly reliably.[47,48]

On the basis of the crystal-chemical analysis of structures belonging to different structural types and containing tetrahedral anions described above, the following algorithm may be proposed for the search for compounds with specified structures and properties.

1. Determination of the projections, layers, or fragments of the structure with the greatest information content for the differentiation of the occupied and free polyhedra and channels.
2. Analysis of the symmetry and the geometrical characteristics of the differentiated polyhedra in the structure (structural types) in order to introduce into the latter new cations by means of isovalent or heterovalent substitution.
3. Establishment of a general crystal-chemical formula taking into account the occupied, free, and partly occupied sites.
4. Modelling of the compositions of the possible compounds by means of isovalent or heterovalent substitutions in the cationic or anionic sublattice taking into account the formal valences and dimensions of the atoms and polyhedra.
5. Comparison of blocks of different structural types in order to achieve their arrangement for the formation of a new structural type (made up of two or several fragments of different structural types) in which the distances between the cations are specified.
6. Estimation of the crystal lattice energy change following the introduction of additional atoms into the basic structure or structural type.
7. Prediction and estimation of the possible properties taking into account the characteristics of the structure.

Depending on the tasks faced by the synthetic chemist, some of the items may be omitted or they may change places, but items 1–4 and 7 are in all cases fundamental for the specific design of new compounds based on crystal-chemical data.

Only one of the possible aspects of the construction of compounds (geometrical and spatial factors) has been considered in the present review. Problems concerning the distortion of crystal lattices, the changes in symmetry, the distribution of cations and electron density in the structure, energetic aspects, and others have been considered only occasionally, mainly for the understanding of the transition from the model to a specific compound. There is no doubt that, in the solution of a problem as complex as the modelling of the compositions, structures, and properties of new phases, many approaches exist which have not been mentioned in this review, for example the methods of energetic crystal chemistry.[208]

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