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The Crystal Structures of Na_2ZnSiO_4, Na_2ZnGeO_4, and Na_2MgGeO_4

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The isotypic compounds Na_2ZnSiO_4, Na_2ZnGeO_4 and Na_2MgGeO_4 derive from orthorhombic β-$NaFeO_2$ ($Pbn2_1$-C^9_{2v}) by cross substitution of the type $M^{II} + M^{IV} = 2\,M^{III}$ and their diffraction lines can be indexed with very similar orthorhombic unit cells. However the ordering of the M^{II} = Zn, Mg and M^{IV} = Si, Ge atoms on the M^{III} = Fe sites lowers the symmetry to Pn or in the standard notation to Pc. The structure type of Na_2ZnSiO_4 is the first example of an ordered quaternary tetrahedral structure related to hexagonal diamond.

Introduction

It has been demonstrated, recently in great detail (Parthé, 1964), that normal tetrahedral structures can form if the average number of valence electrons per atom of the compound is equal to four. We understand under the term of a normal tetrahedral structure a structure where every atom in the structure has four nearest neighbor atoms located approximately at the corners of a surrounding tetrahedron. Using a simple procedure called cross-substitution it is possible, starting from diamond with the simplest tetrahedral structure, to derive theoretically all the possible binary, ternary, quaternary, and more complicated normal tetrahedral structure compositions. The cross-substitution consists of a replacement of an atom pair in the simple structure by two different elements having more and less electrons while keeping the electron to atom ratio constant. If we use the valence electron numbers of the elements to denote the elements we can demonstrate the principle of a cross-substitution by a series of compositions as for example;

$$4 \rightarrow 26 \rightarrow 136_2 \rightarrow 1_2246_4.$$

We know two ideal tetrahedral structures for elements, one is the normal, cubic diamond structure, the other being the hexagonal diamond structure (Bundy and Kasper, 1967). The crystal structure of compounds where the compositions can be derived by cross-substitution should be essentially cubic or hexagonal diamond structures with ordered atom arrangements. Examples are well known for structure types geometrically derived from normal diamond. They are the zinc blende structure type for 26 compounds, the chalcopyrite structure type for 136_2 compounds and the stannite structure type for 1_2246_4 compounds. Not so much is known for structures types derived from hexagonal diamond. The zincite (or wurtzite) structure type occurs with 26 compounds. Bertaut *et al.* (Bertaut and Blum, 1954; Bertaut, Delapalme, and Bassi, 1964) worked out the β-$NaFeO_2$ structure type for 136_2 compounds, but no ordered quaternary structure type related to hexagonal diamond has ever been found. Such a structure type could possibly occur with Na_2ZnSiO_4, Na_2ZnGeO_4 and Na_2MgGeO_4 and it was for this reason why the structural study of these compounds was undertaken.

Sample Preparation

The samples were prepared according to the reaction:

$$Na_2CO_3 + M^{2+}O + M^{4+}O_2 \rightarrow Na_2M^{2+}M^{4+}O_4 + CO_2\uparrow.$$

Mixtures of the oxides with soda were heated on air in porcellan boats. Heating time was 1 day at 500C plus 1 day at 900C plus 4 days at 1050C for Na_2ZnSiO_4, 3 days at 1100C for Na_2MgGeO_4 and 2 days at 700C plus 3 days at 1050C for Na_2ZnGeO_4. The reaction was complete and the final product contained no trace of other phases.

Structure Determination

The powder diffraction patterns of Na_2ZnSiO_4, Na_2ZnGeO_4, and Na_2MgGeO_4 show immediately

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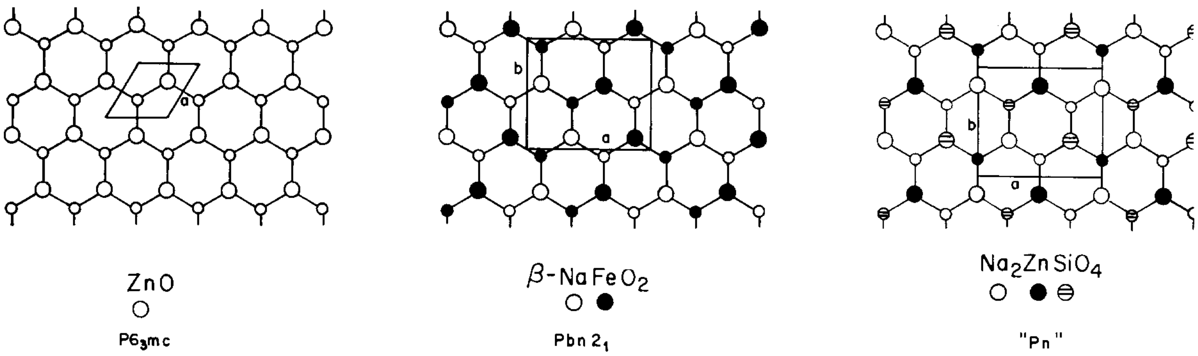

FIG. 1. Projections along the *c* axis for ZnO and the derivative structures of β-$NaFeO_2$ and Na_2ZnSiO_4. For clarity the oxygen atoms are not shown.

that all three compounds are isotypic and also very similar to β-$NaFeO_2$. Based on this similarity it was possible to index all lines of the new patterns with similar orthorhombic unit cells having the following parameters:

Na_2ZnSiO_4: $a = 7.02$ Å $b = 5.44$ Å $c = 5.24$ Å
Na_2ZnGeO_4: $a = 7.17$ Å $b = 5.56$ Å $c = 5.32$ Å
Na_2MgGeO_4: $a = 7.15$ Å $b = 5.60$ Å $c = 5.35$ Å

In comparison the data for β-$NaFeO_2$ with setting $Pbn2_1(C_{2v}^9)$ are:

β-$NaFeO_2$: $a = 7.136$ Å $b = 5.672$ Å $c = 5.377$ Å

While in β-$NaFeO_2$ all reflections *h*0*l* with $h + l = 2n + 1$ and 0*kl* with $k = 2n + 1$ are systematically absent, in the patterns of the quaternary compounds weak 0*kl* reflections with $k = 2n + 1$ were observed, the only systematic extinctions being then *h*0*l* with

TABLE I

UNIT CELL VECTORS AND IDEALIZED ATOM POSITIONS FOR THE TETRAHEDRAL STRUCTURE MODEL FOR Na_2ZnSiO_4

Pseudo orthorhombic cell "Pn"	First monoclinic cell Pc	Second monoclinic cell Pc
	Unit cell vectors	
$\mathbf{a}_O(\sim 2a_{\text{wurtzite}})$	$\mathbf{a}_{M_1} = \mathbf{a}_O$	$\mathbf{a}_{M_2} = \mathbf{a}_O - \mathbf{c}_O\left(\sim\frac{\sqrt{20}}{\sqrt{3}}a_{\text{wurtzite}}\right)$
$\mathbf{b}_O(\sim\sqrt{3}\,a_{\text{wurtzite}})$	$\mathbf{b}_{M_1} = \mathbf{b}_O$	$\mathbf{b}_{M_2} = \mathbf{b}_O$
$\mathbf{c}_O(\sim c_{\text{wurtzite}})$	$\mathbf{c}_{M_1} = -\mathbf{a}_O + \mathbf{c}_O\left(\sim\frac{\sqrt{20}}{\sqrt{3}}a_{\text{wurtzite}}\right)$	$\mathbf{c}_{M_2} = \mathbf{c}_O$
	$tg\beta = -\frac{a_O}{c_O}$	$tg\beta = -\frac{c_O}{a_O}$
	$(\beta \sim 140.8°)$	$(\beta \sim 129.2°)$
	Idealized parameters	
$xyz,\ x + \frac{1}{2}\bar{y}z + \frac{1}{2}$	$xyz,\ x\bar{y}z + \frac{1}{2}$	$xyz,\ x\bar{y}z + \frac{1}{2}$
2 Na with $x = \frac{3}{4}$, $y = \frac{2}{3}$, $z = 0$	2 Na with $x = \frac{3}{4}$, $y = \frac{2}{3}$, $z = 0$	2 Na with $x = \frac{3}{4}$, $y = \frac{2}{3}$ $z = \frac{3}{4}$
2 Na with $x = \frac{1}{2}$, $y = \frac{1}{6}$, $z = 0$	2 Na with $x = \frac{1}{2}$, $y = \frac{1}{6}$, $z = 0$	2 Na with $x = \frac{1}{2}$, $y = \frac{1}{6}$, $z = \frac{1}{2}$
2 Zn with $x = 0$, $y = \frac{1}{6}$, $z = 0$	2 Zn with $x = 0$, $y = \frac{1}{6}$, $z = 0$	2 Zn with $x = 0$, $y = \frac{1}{6}$, $z = 0$
2 Si with $x = \frac{1}{4}$, $y = \frac{2}{3}$, $z = 0$	2 Si with $x = \frac{1}{4}$, $y = \frac{2}{3}$, $z = 0$	2 Si with $x = \frac{1}{4}$, $y = \frac{2}{3}$, $z = \frac{1}{4}$
2 O with $x = \frac{3}{4}$, $y = \frac{2}{3}$, $z = \frac{3}{8}$	2 O with $x = \frac{1}{8}$, $y = \frac{2}{3}$, $z = \frac{3}{8}$	2 O with $x = \frac{3}{4}$, $y = \frac{2}{3}$, $z = \frac{1}{8}$
2 O with $x = \frac{1}{2}$, $y = \frac{1}{6}$, $z = \frac{3}{8}$	2 O with $x = \frac{7}{8}$, $y = \frac{1}{6}$, $z = \frac{3}{8}$	2 O with $x = \frac{1}{2}$, $y = \frac{1}{6}$, $z = \frac{7}{8}$
2 O with $x = 0$, $y = \frac{1}{6}$, $z = \frac{3}{8}$	2 O with $x = \frac{3}{8}$, $y = \frac{1}{6}$, $z = \frac{3}{8}$	2 O with $x = 0$, $y = \frac{1}{6}$, $z = \frac{3}{8}$
2 O with $x = \frac{1}{4}$, $y = \frac{2}{3}$, $z = \frac{3}{8}$	2 O with $x = \frac{5}{8}$, $y = \frac{2}{3}$, $z = \frac{3}{8}$	2 O with $x = \frac{1}{4}$, $y = \frac{2}{3}$, $z = \frac{5}{8}$

$h + l = 2n + 1$. The diffraction symmetry contained in the quaternary structures is thus only a *n*-glide perpendicular to the *b* direction, which, provided that the structure has orthorhombic symmetry, would indicate space group $Pmn2_1(C^7_{2v})$ or $Pmnm(D^{13}_{2h})$ which is centro-symmetric and ruled out by a positive piezo electric test.

The similarity of the diffraction patterns to that of β-$NaFeO_2$ let us assume that the structure of the quaternary compounds is the same as that of β-$NaFeO_2$, except that now an Fe atom pair is replaced by one element of Group 2, like Zn or Mg, and one element of Group 4, like Si or Ge. In Fig. 1 are shown projections along the *c* axis for the ZnO structure, for the β-$NaFeO_2$ structure and for a model for the structure of Na_2ZnSiO_4, derived according to the above discussed scheme. For clarity the O atoms which are everywhere placed on top of the metal atoms have been omitted from the drawing. The model structure for Na_2ZnSiO_4 contains the *n*-glide perpendicular to the *b*-direction, however the symmetry is not anymore orthorhombic, but only pseudo-orthorhombic. If we insist on using the same orthogonal cell the apparent space group is Pn, which is a space group not listed as such in the International Tables. Agreement with the latter is obtained if a new set of monoclinic axes is chosen and the space group of Na_2ZnSiO_4 can then be written as Pc. There are two different monoclinic unit cells which could be chosen with equal justification. In Table I are listed the unit cell vector equations and the idealized point positions for the Na_2ZnSiO_4 model structure for the pseudo-orthorhombic and the two monoclinic unit cells.

A comparison of the powder diffraction intensities with the intensities calculated for the structure model showed that the latter was essentially correct but needed refinement. To obtain accurate powder intensity values a diffractometer chart was recorded on drawing paper. Each diffraction peak was then cut out and the paper weighted on a microbalance. The intensity values corrected for Lorentz and polarization factor were then used in a special refinement program written by Dr. Bassi. The particular feature of the program is the possibility to use also intensity packets of coinciding diffraction lines, a feature which was of great importance here.

The final parameters for Na_2ZnSiO_4 with a reliability factor of 15% are shown in the left hand part of Table II. The agreement between calculated and observed *d* values and $p \cdot F^2$ values can be studied in Table III.

Comparison between the Different Structure Proposals

At this time in our research work we received notice of a Russian single crystal study on Na_2ZnSiO_4 by Ilyukhin, Nikitin, and Belov (1967). Their unit cell dimensions for Na_2ZnSiO_4 with "Pn" setting are:

$$a = 7.02 \text{ Å} \quad b = 5.48 \text{ Å} \quad c = 5.33 \text{ Å and } \beta = 90°20'$$

in essential agreement with our data. Their atomic point positions, also with a reliability factor of 15%, are given on the right hand side of Table II. There is in general an agreement between our and the Russian results except for the *z* parameter of O_I and the *y* parameter of O_{IV}. These changes are, however, big enough to conceal the geometrical relationship of the quaternary structure to the hexagonal diamond

TABLE II

ATOMIC PARAMETERS FOR Na_2ZnSiO_4 (Setting "Pn")

	This work			Ilyukhin, Nikitin and Belov (1967)		
			$xyz, x + \frac{1}{2}\bar{y}z + \frac{1}{2}$			
2 Na_I	0.746	0.695	0.997	0.743	0.686	0.978
2 Na_{II}	0.505	0.177	0.997	0.504	0.185	0.980
2 Zn	0.003	0.192	0.999	0.000	0.168	0.000
2 Si	0.245	0.688	0.000	0.249	0.686	0.006
2 O_I	0.724	0.601	0.435	0.723	0.604	0.547
2 O_I	0.556	0.154	0.437	0.564	0.188	6.391
2 O_{III}	0.935	0.221	0.359	0.944	0.251	0.357
2 O_{IV}	0.286	0.689	0.302	0.283	0.800	0.281

TABLE III

CALCULATED AND OBSERVED d-VALUES AND $p \cdot F^2$ VALUES FOR Na_2ZnSiO_4 (CuK_α RADIATION)

hkl^a	hkl^b	d_{calc}	d_{obs}	$p \cdot F^2_{calc} \cdot 10^{-2}$			$p \cdot F^2_{obs} \cdot 10^{-2}$
010	010	5.44	5.45		0.9		1.0
$11\bar{1}$	$110, 1\bar{1}0$	4.30	4.30		70.6	154.9	144.9
100	101	4.20	4.22	40.3	84.3		
$10\bar{2}$	$10\bar{1}$			44.0			
011	$011, 01\bar{1}$	3.774	3.78		20.5		16.1
$20\bar{2}$	200	3.510	3.53		14.8		14.0
110	$111, 1\bar{1}1$	3.324	3.33	11.1	18.2		13.7
$11\bar{2}$	$11\bar{1}, \bar{1}11$			7.1			
$21\bar{2}$	$210, 2\bar{1}0$	2.949	2.957		143.4		150.6
020	020	2.720	2.712		180.4		175.6
002	002	2.620	2.634		254.1		262.3
$21\bar{1}$	$211, 2\bar{1}1$	2.570	2.575	232.7	457.5	462.5	524.8
$21\bar{3}$	$21\bar{1}, \bar{2}11$			224.8			
$12\bar{1}$	$120, 1\bar{2}0$	2.536	2.533		5.0		
021	$021, 02\bar{1}$	2.414	2.412		90.8		72.8
012	$012, 01\bar{2}$	2.361	2.360		6.8		3.4
120	$121, 1\bar{2}1$	2.283	2.279	13.8	46.5		33.7
$12\bar{2}$	$12\bar{1}, \bar{1}21$			32.7			
111	$112, 1\bar{1}2$	2.237	2.239	7.7	47.6		38.5
$11\bar{3}$	$11\bar{2}, \bar{1}12$			39.9			
$22\bar{2}$	$220, 2\bar{2}0$	2.150	2.149		26.2	89.8	75.6
$31\bar{3}$	$310, 3\bar{1}0$	2.149			22.7		
$30\bar{2}$	301	2.136		38.4	40.9		
$30\bar{4}$	$30\bar{1}$			2.5			
200	202	2.100	2.104	22.8	53.8		36.7
$20\bar{4}$	$20\bar{2}$			31.0			
$22\bar{1}$	$221, 2\bar{2}1$	1.989	1.992	30.2	47.7	216.8	202.5
$22\bar{3}$	$22\bar{1}, \bar{2}21$			17.5			
$31\bar{2}$	$311, 3\bar{1}1$	1.988		16.7	33.7		
$31\bar{4}$	$31\bar{1}, \bar{3}11$			17.0			
210	$212, 2\bar{1}2$	1.959	1.963	68.9	135.4		
$21\bar{4}$	$21\bar{2}, \bar{2}12$			66.5			
022	$022, 02\bar{2}$	1.887	1.881		148.5		166.1
121	$122, 1\bar{2}2$	1.822	1.812	2.3	22.2	36.5	13.6
$12\bar{3}$	$12\bar{2}, \bar{1}22$			19.9			
030	030	1.813			14.3		
$32\bar{3}$	$320, 3\bar{2}0$	1.774	1.763		22.2	257.5	273.8
$13\bar{1}$	$130, 1\bar{3}0$	1.756			31.4		
$40\bar{4}$	400	1.755			203.9		
031	$031, 03\bar{1}$	1.714	1.714		0.8		4.1
102	103	1.695	1.697	56.7	69.7	132.0	121.5
$10\bar{4}$	$10\bar{3}$			13.0			
$32\bar{2}$	$321, 3\bar{2}1$	1.6802	1.684	54.2	59.5		
$32\bar{4}$	$32\bar{1}, \bar{3}21$			5.3			
$41\bar{4}$	$410, 4\bar{1}0$	1.6702			2.8		

[a] First monoclinic unit cell: $a = 7.02$; $b = 5.44$; $c = 8.76$; $\beta = 143.26°$.

[b] Triclinic, pseudo-orthorhombic unit cell: $a = 7.02$; $b = 5.44$; $c = 5.24$.

structure with the Russians reporting that one Na atom has a distorted octahedral and the other an unusual 5-fold coordination. According to our results the structure, although slightly distorted, is truly a tetrahedral structure with every atom having four tetrahedral neighbors at reasonable interatomic distances: Zn–O = 1.95 Å(4×); Si–O = 1.61 Å(4×); Na_1–O = 2.35 Å(4×) and Na_2–O = 2.33 Å(4×).

As stated before, both the parameters obtained by Belov *et al.* and those obtained by us have the same reliability index. In general, one has greater confidence in data obtained from single crystal experiments. Nevertheless, the unusual coordination for Na reported by the Russians as compared to our results and our logical derivation of the Na_2ZnSiO_4 structure from the β-$NaFeO_2$ structure places perhaps a shadow of a doubt on the correctness of the Russian parameters and makes it highly desirable to have Na_2ZnSiO_4 reinvestigated using single crystal diffraction methods.

Other Isotypic Compounds

No structure refinement has been made on Na_2ZnGeO_4 and Na_2MgGeO_4, however, an intensity calculation using the adjustable parameters for Na_2ZnSiO_4 has shown agreement between observed and calculated intensity values. Due to the different size of the atoms as compared to Na_2ZnSiO_4, there will certainly be small changes of the adjustable parameters, however, the structure type for all three compounds is the same. In analogy to β-$NaFeO_2$, which undergoes a phase change at 1100C, we found, using thermal analsyis, a high temperature transformation with Na_2ZnSiO_4 at 998 ± 4C and Na_2ZnGeO_4 at 1156 ± 4C. The data for Na_2MgGeO_4 are inconclusive. If there is a phase transformation it will be very close to the melting point of Na_2MgGeO_4 which we determined to be at 1178 ± 4C.

Discussion

The structure of Na_2ZnSiO_4 is an example of an ordered quaternary tetrahedral structure based on the hexagonal diamond structure. From the point of view of the systematization of crystal structures the present study illustrates the usefulness of the concepts of valence electron concentration (Parthé, 1964) and of cross substitution and shows interesting filiations in oxides: C diamond (hexagonal)—ZnO (hexagonal)—$\gamma LiAlO_2$ (tetragonal) (Bertaut, Delapalme, Bassi, Durif-Varambon, and Joubert, 1965)—$\beta FeNaO_2$ (orthorhombic)—Na_2ZnSiO_4 (monoclinic) to take place with a continuous lowering of symmetry.

Theoretically we can predict that only those ordered atom arrangements should occur with tetrahedral structures which require a minimum of electron shift for the necessary sp^3 hybridization of all the atoms. This leads, in the case of quaternary compounds of composition A_2BCD_4, to two simple atom arrangements; one is the arrangement given here for monoclinic Na_2ZnSiO_4, the other one was recently found with Cu_2CdGeS_4 which has the same relative cell dimensions as the pseudo-orthorhombic Na_2ZnSiO_4 but in effect truly orthorhombic symmetry (Parthé, Yvon, and Deitch, 1969). The limited experimental evidence seems to indicate that the monoclinic structure type is preferred with compounds containing oxygen anions, while the orthorhombic structure type is found with S and Se compounds.

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