CRYSTAL STRUCTURE OF

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Abstract

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CRYSTAL STRUCTURE OF

$K_2Mn_2Zn_4Si_4O_{15} = K_2Mn_2Zn_4[SiO_4]_2[Si_2O_7]$

The crystal phosphor $K_2Mn_2Zn_4Si_4O_{15}$ was obtained at the Institute of Geology and Geophysics of the Siberian Branch of the Academy of Sciences of the USSR by G. V. Bukin by a hydrothermal method in the temperature range 580-600° at a pressure of 800 atm. The charge was selected in the ratio $ZnO : SiO_2 : KCl : KOH : MnCl_2 = 5 : 5 : 9 : 1 : 1$. In the study of the optical properties of the synthesized crystals, phosphorescence in the red part of the spectrum was clearly manifested, and, in order to explain the peculiar luminescent properties of this compound, it was of interest to solve its atomic structure, in particular the crystallographic position and coordination of the manganese atoms, since the incorporation into the structure of Mn atoms is characteristic of luminescent zinc silicates, isomorphously replacing Zn ([1]).

The x-ray experimental material used consisted of 326 independent reflections from five ($hk0$—$hk4$) x-ray goniometric layer-line photographs, $\max \sin\vartheta/\lambda = 0.9$ (Mo radiation). The intensities of the reflections were estimated according to the $\sqrt[4]{2}$ scale of blackenings recorded from the crystal. The parameters of the rhombic cell, determined from rotation-oscillation x-ray photographs and refined on a DRON single-crystal diffractometer, are:

$$a = 8.944 \pm 0.002\ \text{Å},$$
$$b = 15.834 \pm 0.002\ \text{Å},$$
$$c = 5.205 \pm 0.004\ \text{Å};$$
$$\rho = 3.48\ \text{g/cm}^3.$$

The chemical-analysis data led to the formula $K_2Mn_2Zn_4Si_4O_{15}$. The unit cell contains two units of the indicated composition. The systematic extinctions allowed four space groups: $Immm$, $I222$, $I2_12_12_1$, and $Imm2$. In the three-dimensional distribution of the function $P(uvw)$, only one peak on the $00w$ axis at a very small period c excluded the holohedral $Immm$. The results of atom localization on the basis of the three-dimensional Patterson function gave

Fig. 1. $K_2Mn_2Zn_4[Si_4O_{15}]$. *xy*-projection of the electron-density distribution

Figure 1: Fig. 1. $K_2Mn_2Zn_4[Si_4O_{15}]$. *xy*-projection of the electron-density distribution

Figure 2

Figure 2: Figure 2

no grounds for rejecting the group

$$Imm2 = Im(n)m(n)2(2_1).$$

From the three-dimensional Patterson function the Zn and Mn atoms were fixed; their distinction was aided by the different multiplicity ($8:4$) of the corresponding positions in the group $Imm2$. The remaining atoms were revealed by a cycle of successive approximations.

Fig. 1. $K_2Mn_2Zn_4[Si_4O_{15}]$. *xy*-projection of the electron-density distribution.

The *xy*-projection of the electron-density distribution is shown in Fig. 1. All calculations were carried out at the Computing Center of Moscow University using programs of the Institute of Chemical Physics of the Academy of Sciences of the USSR ([2]). The assembled model was refined by the least-squares method (LSM) down to a minimum value of the R_{hkl}-factor of 13.5%. The coordinates of two oxygen atoms (O_1 and O_6) could not be refined by LSM, which may be associated with the arrangement of most of the heavy atoms at the zero and half levels and with the appearance in the structure of a pseudo-plane of symmetry perpendicular to the *z*-axis, which hindered refinement of the light oxygen atoms. In addition, the atoms O_1 and O_6 are the nearest neighbors of the Mn atom, whose polarizing influence also hampers refinement of their positions, fixed from the three-dimensional synthesis of electron density. The final coordinate values of the basis atoms are given in Table 1.

Fig. 2. $K_2Mn_2Zn_4[SiO_4]_2[Si_2O_7]$. "Ribbed" dimetanets $[Zn_2O_5]_{\infty\infty}$, centered by $[SiO_4]$ tetrahedra (stretched onto the glide plane coincident with the plane of the drawing and therefore with two orientations of the components). Along the short *z*-axis, metachains $[Zn_2O_6]_{\infty}$, encrusted with Si orthotetrahedra common to two Zn chains, stand out. Along *x*, chains of the willemite type are visible, in which pairs of Zn tetrahedra alternate with one Si tetrahedron.

The principal architectural detail of the deciphered K, Mn, Zn silicate may be regarded as a network of tetrahedra with hexagonal loops of the best-known type, perpendicular to the *y*-axis (Fig. 2), but in the oxygen tetrahedra the Zn atoms are located. With the normal dimeta formula $[Zn_2O_5]_{\infty\infty}$, the networks look identical on both sides (they are "stretched" onto a plane with glide *n*); in each ring four tetrahedra face in one direction, and in neighboring rings in the opposite direction ("ribbed networks," Fig. 2 and more clearly in Fig. 3, cf. ([3])). In

Fig. 3

Figure 3: Fig. 3

this network motif, along [001] one readily distinguishes its metachains of the pyroxene type $[Zn_2O_6]_\infty$. They are similar to those repeatedly fixed in Zn minerals, where the chains are usually encrusted with orthotetrahedra: $[SiO_4]$-tetrahedra in hodgkinsonite and clinohedrite ([4,5]), $[PO_4]$—in hopeite—phosphophyllite ([6,7]). In the structure under consideration, the metachains twisting around the 2_1 axes are also encrusted with ortho-

Table 1

Coordinates of the basis atoms of the structure $K_2Mn_2Zn_4Si_4O_{15}$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Zn	0.191	0.192	0	O_2	0.153	0.234	0.617
Mn	0.148	0	0.631	O_3	0	0.206	0.203
K	0.5	0.117	0.415	O_4	0.5	0	0.025
Si_1	0	0.192	0.501	O_5	0.250	0.079	0.939
Si_2	0.322	0	0.069	O_6	0.302	0	0.376
O_1	0	0.083	0.495				

tetrahedra $[SiO_4]$, but each $[SiO_4]$, being located in a mirror plane, simultaneously participates—incrusts two metachains $[Zn_2O_6]_\infty$; in other words, the Si orthotetrahedra center all the rings of the net made of Zn tetrahedra. Obeying the clinoplanarity n, these $[SiO_4]$ bands face alternately in one direction and the other along the y axis (Figs. 2 and 3)*.

It is very interesting that in the nets $[Zn_2O_5]_{\infty\infty}$ of the structure under consideration (Fig. 2) one can distinguish chains of the willemite (Zn_2SiO_4) type parallel to the y axis, i.e., in them two Zn tetrahedra alternate with one Si tetrahedron.

Fig. 3. $K_2Zn_4[Si_2O_7]Mn_2[SiO_4]_2$.
a—mechanism by which the discrete nets $[Zn_2O_5]_{\infty\infty}$ are joined into a framework by means of dinuclear groups (Mn_2O_8) (in the narrow parts of the corridors between layers), alternating with diorthogroups $[Si_2O_7]$ in a single wavy chain; *b*—second projection of the wavy chain made up of alternating groups (Mn_2O_8) and $[Si_2O_7]$.

In willemite such chains twist in three turns around the screw axis 3_1 ([9]), whereas in the Zn, Mn silicate under consideration they twist in two turns around a (pseudo) double screw axis 2_1.

The second half of the silica component represented in the formula participates in the structure under consideration in the form of island diorthogroups $[Si_2O_7]$, as was noted earlier for synthetic zinc silicate (^{10}) and for the beryllosilicates —barylites (^{11}) and bertrandite (^{12}), which are usually close to Zn silicates; however, in these structures there is no second type of silicon-oxygen radical— there are no orthogroups.

Located at the intersection of two mirror planes, the diorthogroups serve as an openwork linkage (along y) between the discrete nets $[Zn_2O_5]_{\infty\infty}$. The diorthogroups elongated along the x axis are polar: their vertices face in one direction along the z axis (Fig. 3).

Of particular interest in the structure under consideration is the role of the Mn atoms, which, in their coordination polyhedra, alternating with diorthogroups in the common mirror plane m (010), also participate (Fig. 3) in linking neighboring dimetal layers (in the narrower parts of the corridors between the walls). The Mn polyhedra are five-vertex semioctahedra; they are paired through a common edge (from the pseudoquadratic base, Fig. 3) into groups (Mn_2O_8). In connection with the assumption that the optical features of the deciphered Mn, Zn silicate are related to the Mn component, it may be noted that in the recently analyzed ^{13} synthetic $Na_2Mn_2[Si_2O_7]$, half of the Mn (Mn_{II}) also has fivefold coordination, but in the form of a trigonal bipyramid, pairs of such bipyramids being joined through a common lateral edge into (Mn_2O_8). Further, however, these groups, by means of Mn_I-tetrahedra, are built up into infinite ribbons, whereas in the Zn,Mn silicate the pairs (Mn_2O_8), while remaining isolated (from one another) by links of discrete $[Zn_2O_5]_\infty$-layers, alternate in this role with orthogroups $[Si_2O_7]$ in a single wavy ribbon with a common direction along the x axis (Fig. 3). Through the (polar) vertices of the orthogroups $[Si_2O_7]$ and the (apical) vertices of the Mn half-octahedra, these ribbons are linked into a very open network, parallel to the principal nets $[Zn_2O_5]_\infty$. The common edge of two Mn half-octahedra connects the orthogroups $[SiO_4]$ from neighboring Zn nets.

Table 2

Interatomic distances (in Å) in the structure of $K_2Mn_2Zn_4Si_4O_{15}$

Si_1-tetrahedron	Si_2-tetrahedron	Zn-tetrahedron	Mn-half-octahedron
$Si_1—O_1$ 1.72	$Si_2—O_4$ 1.61	$Zn—O_2$ 2.14	$Mn—O_1$ 1.99
$Si_1—O_2$ 1.64	$Si_2—O_5$ 1.56	$Zn—O''_2$ 1.92	$Mn—O'_1$ 1.99
$Si_1—O'_2$ 1.64	$Si_2—O'_5$ 1.56	$Zn—O_3$ 2.02	$Mn—O_5$ 2.22
$Si_1—O_3$ 1.56	$Si_2—O_6$ 1.60	$Zn—O_5$ 1.90	$Mn—O_5$ 2.22
Avg. 1.64	Avg. 1.58	Avg. 1.99	$Mn—O'_6$ 1.91
$O_1—O_3$ 2.48	$O_4—O_6$ 2.56	$O_2—O''_2$ 3.33	**K-octahedron**

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* In an analogous manner, $[SiO_4]$-tetrahedra center strictly hexagonal nets of Li tetrahedra in the structure of Li_2SiO_3, but there (^{8}) all the tetrahedra (Li and Si) are oriented identically.

Si_1-tetrahedron	Si_2-tetrahedron	Zn-tetrahedron	Mn-half-octahedron
O_1—O_2 2.82	O_5—O_6 2.64	O_2''—O_5 3.20	K—O_6 2.57
O_1—O_2' 2.82	O_5'—O_6 2.64	O_2''—O_3 3.30	K—O_4 2.74
O_2—O_2' 2.74	O_4—O_5 2.60	O_2—O_5 3.50	K—O_6' 2.57
O_2—O_3 2.58	O_4—O_5' 2.60	O_5—O_3 3.30	K—O_3 3.20
O_3—O_2' 2.58	O_5—O_5' 2.60	O_2—O_3 3.37	K—O_2'' 3.10
			K—O_2''' 3.10

In the channels formed between the Zn layers and the $[Si_2O_7]$ groups there are large K atoms in deformed octahedra, also paired by a symmetry plane.

All interatomic distances within the coordination polyhedra are given in Table 2. At the present stage of refinement they agree well with the values usually quoted.

Returning to the comparison of the structures of $Na_2Mn_2[Si_2O_7]$ and $K_2Mn_2Zn_4[SiO_4]_2[Si_2O_7]$, one may suppose that identical regions of luminescence are associated with groups (Mn_2O_8) common to both compounds. As noted in [14], for compounds with Mn in tetrahedral coordination green luminescence is characteristic (willemite–troostite), but when the coordination number increases to 6 the luminescence becomes red (rhodonite, helvite). Apparently, red luminescence is also characteristic of Mn^{2+} in fivefold coordination, if its polyhedra are connected into "binuclear" complexes with a pair of Mn atoms at short distances. In $Na_2Mn_2Si_2O_7$ this distance is 3.5 Å; in the Zn,Mn silicate it is 3 Å.

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REFERENCES

1. V. V. Ilyukhin, A. V. Nikitin, N. V. Belov, DAN, 171, No. 6, 1326 (1966).
2. B. L. Tarnopol' skii, V. I. Andrianov, ZhSKh, 4, 434 (1963).
3. R. N. Douglass, Am. Miner., 43, 517 (1958).
4. L. P. Solov' eva, N. V. Belov, DAN, 152, No. 2, 327 (1963).

5. A. V. Nikitin, N. V. Belov, DAN, 148, No. 6, 1386 (1963).
6. R. S. Gamidov, V. P. Golovachev et al., DAN, 150, No. 2, 381 (1963).
7. W. Kleber, F. Liebau, E. Piatkowiak, Acta crystallogr., 14, 795 (1961).
8. B. A. Maksimov, Yu. A. Kharitonov, V. I. Ilyukhin, N. V. Belov, DAN, 178, No. 6 (1968).
9. N. V. Belov, Mineralogich. sborn. L' vovsk. geol. obshch., No. 16, 1962.
10. S. T. Amirdov, A. V. Nikitin, V. V. Ilyukhin, N. V. Belov, DAN, 177, No. 1, 92 (1967).
11. K. K. Abrashev, V. V. Ilyukhin, N. V. Belov, Kristallografiya, 9, No. 6, 816 (1964).
12. L. P. Solov' eva, N. V. Belov, DAN, 140, No. 3, 685 (1961); Kristallografiya, 9, No. 4, 551 (1964).
13. L. P. Astakhova, E. A. Pobedimskaya, V. I. Simonov, DAN, 173, No. 6, 1401 (1967).
14. S. H. Linwood, W. A. Weyl, J. Opt. Soc. Am., 32, No. 8, 443 (1942).

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