

ATOMIC STRUCTURE AND ISOMORPHISM OF SILLENITES $\text{Bi}_{12} \text{M}_x \text{O}_{20 \pm \delta}$

S. F. RADAEV, AND V. I. SIMONOV

Institute of Crystallography, USSR Acad. Sci., Moscow

This structural study was aimed at the investigation of sillenites $\text{Bi}_{12} \text{M}_x \text{O}_{20 \pm \delta}$, with various M cations. Sillenites have cubic symmetry, space group I23. These compounds are interesting because of their physical properties, such as photorefraction, piezoelectricity, optical activity, photoconductivity, etc. That is why they are widely used in holography, piezotechnology, acousto- and optoelectronics.^{1,2} Besides, sillenites exhibit remarkable M cation isomorphism. In these crystals M site can be occupied by cations whose ionic radii differ by a factor of 2 and even more, that ensures control of physical properties of sillenites. Then, of principal importance is the establishment of mechanisms of isomorphous replacements in sillenites.

Up to now only six compounds out of 40 representatives of this crystal class have been investigated. It should be noted that the method of X-ray structural analysis was applied in these studies. The structural model of sillenites suggested in³ has been accepted in the literature. The model is based on X-ray structural studies of crystals with $\text{M} = (\text{Bi}, \text{Fe}), (\text{Bi}, \text{Zn})$. The main idea of the model is as follows. The exact number of O atoms per formula unit in sillenites is 20, the exact valence of M cation or isomorphous cationic mixture at this site equals 4. In the sillenites in which M sites are partially occupied by Bi atoms, the latter have the valence 5+. Thus, the general chemical formula of all the sillenites suggested in³ is $\text{Bi}_{12} \text{M} \text{O}_{20}$. However, the above model contradicts several experimentally established facts, for instance, up to now no reliable data on the presence of pentavalent bismuth in sillenites is available. Our structural studies of sillenites have proved that the model suggested in³ needs to be revised.

We chose for our structural studies the sillenites of various types, 1) sillenites with M cations consisting of one element only $\text{M} = \text{Ge}, \text{Ti}$; 2) si-

lilenites with 'statistic' M-cations $M = (\text{Fe}, \text{P}), (\text{Bi}, \text{Ga}), (\text{Bi}, \text{Fe}), (\text{Bi}, \text{Zn})$ and (Bi, V) . As far as the sillenites of the first group are concerned, of special importance is to establish whether the structures are M cation defective. As for the second group, the main question is to establish the atomic in which M sites are partially populated by Bi atoms the valence of this cation should be found. The application of neutron diffraction allows one to avoid major difficulties that arise during X-ray structural analysis. A strong absorption of X-ray radiation ($\mu = 100 \text{ mm}^{-1}$ for $\text{MoK}\alpha$) hinders its correct allowance, the error in the determination of linear dimensions of a sample affects the parameters of atomic thermal motion. Besides, the presence of a large number of strongly scattering Bi ($Z = 83$) prevents ready determination of structural characteristics of light atoms. The problems of the correlation between occupancy coefficients and the parameters of atomic thermal motion become crucial. We have carried out a very accurate X-ray structural analysis of Ge-sillenite to elucidate the possibilities of an X-ray technique.⁴ In that study we made allowance for absorption, extinction, thermal diffuse scattering, the final R-factors were $R_w = 1.61$ and $R = 1.77\%$. That study showed that a reliable determination of such structural parameters as occupancy of atomic sites is impossible if X-ray analysis is applied. R-factors are not sensitive to a variation of O site occupancy in the range $q = 0.70 - 1.20$ (in this case B_{O} varies from 0.41 to 1.72 Å) due to insignificant scattering and a strong correlation between the occupancy and thermal parameters. An advantage of applying neutron diffraction technique consists in the fact that neutron scattering by Bi and O atoms is comparable, that makes the determination of structural characteristics of O atoms much more reliable. Neutron diffraction measurements were made on a VVERTS reactor of a branch Karpov Institute of Physical Chemistry on a Syntex P $\bar{\text{T}}$ diffractometer, $\lambda = 1.167 \text{ \AA}$, Cu-monochromator, $\vartheta/2\vartheta$ - scan mode, in a reciprocal space hemisphere $h \geq 0$ to $\sin \vartheta/\lambda = 0.79 \text{ \AA}^{-1}$, with the assistance of V. A. Sarin, E. E. Rider, V. N. Kanepit. The main crystal data and experimental results are listed in Table 1. The atomic neutron scattering lengths were: $b_{\text{Bi}} = 8.5256 (14)$, $b_{\text{O}} = 5.805 (4)$, $b_{\text{Ge}} = 8.1929 (17)$, $b_{\text{Ti}} = -3.30 (2)$, $b_{\text{Fe}} = 9.54 (6)$, $b_{\text{P}} = 5.13 (1)$, $b_{\text{Ga}} = 7.288 (10)$, $b_{\text{V}} = -0.3824 (12)$, $b_{\text{Zn}} = 5.680 (5) \text{ fm}$. All the calculations were made using the PROMETHEUS program system.⁵ No absorption correction was made because μR did not exceed 0.01.

The first X-ray structural studies of single crystals of sillenites with M cations consisting of one element only, $\text{Bi}_{12} \text{GeO}_{20}$ and $\text{Bi}_{12} \text{SiO}_{20}$, were made by Abrahams et al.^{6,7} These structural data are often used to explain the physical characteristics of sillenites.^{8,9} However, a more detailed analysis of the structural information given in^{6,7} makes some of those results

Table 1. Experimental and crystal data.

Chemical formula	Sample	a , Å	n_{obs}	n_{uniq}	R_w , %	R , %
$Bi_{12}GeO_{20}$	Ø 6.7	10.153 (4)	3655	377	2.01	1.73
$Bi_{12}Ti_{0.90}O_{19.80}$	Ø 6.2	10.186 (3)	4069	395	1.90	1.58
$Bi_{12}(Fe_{0.35}P_{0.59}\square_{0.06})O_{20}$	4.0 x 4.0 x 6.0	10.167 (14)	2780	300	1.69	1.76
$Bi_{12}(Bi_{0.50}Ga_{0.50})O_{19.50}$	Ø 4.3	10.183 (3)	3779	375	1.58	1.31
$Bi_{12}(Bi_{0.50}Fe_{0.50})O_{19.50}$	Ø 5.7	10.184 (69)	3836	375	1.87	1.73
$Bi_{12}(Bi_{0.67}Zn_{0.33})O_{19.33}$	Ø 5.1	10.207 (3)	3513	354	1.70	1.61
$Bi_{12}(V_{0.89}Bi_{0.03}\square_{0.08})O_{20.27}$	2.6 x 3.8 x 5.6	10.247 (8)	3042	312	1.69	1.52

doubtful. The occupancies of M sites reported in^{6,7} are $q_{Ge} = 0.87$ (2), $q_{Si} = 0.87$ (8). In this case the thermal parameters of appropriate atoms were anomalously low $B_M \leq 0.18 \text{ \AA}^2$, that is one fifth the value of the remainder atoms within the structure. One can suppose that the results are not true due to a strong correlation between the occupancy coefficient q_M and the thermal parameter B_M of M the atom. It is due to this strong correlation that Ti site occupancy was not refined in,¹⁰ reporting an X-ray structural study of $Bi_{12}TiO_{20}$.

The refinement of structural models of $Bi_{12}GeO_{20}$ and $Bi_{12}TiO_{20}$ and the analysis of nuclear density maps did not reveal any essential peculiarities as compared to the geometry of the model suggested in.⁶ The main task was to reveal possible vacancies in tetrahedral M cationic sites. Erroneous, to our mind, results given in⁶ ($q_{Ge} = 0.87$ (2)) could be obtained without allowance for a strong correlation between q and B parameters. To refine the structural models with strongly correlating parameters we have been successfully using quite for a long time a step-by-step scanning technique.¹¹ It consists in constructing a section of a minimized functional R_w from one of the strongly correlating parameters by a trial-and-error method and ISM refinement. To do this, a series of refinements of the remaining structure parameters is carried out for fixed values of one of the strongly correlating parameters. Thus, it is possible to estimate the true errors in determining these parameters and choose the most probable values of the parameters sometimes using supplementary information (physical, crystal-chemical, etc.). The results of such a procedure for Ge- and Ti-sillenites are shown in Fig. 1, presenting R_{wmin} sections depending on occupancy factor q of M atoms (Fig. 1a) and $O(3)$ atoms of the tetrahedral environment of the M-cation (Fig. 1b). For Ge-sillenite the minima $R_w(q_{Ge})$ and $R_w(q_{O(3)})$ (curves 1 in Fig. 1a, b) are vivid and they practically coincide with the values $q_{Ge} = 1.00(3)$ and $q_{O(3)} = 1.00(3)$, the thermal parameters of these atoms being $B_{Ge} = 0.51$ (2) and $B_{O(3)} = 1.10$ (2) \AA^2 . In ot-

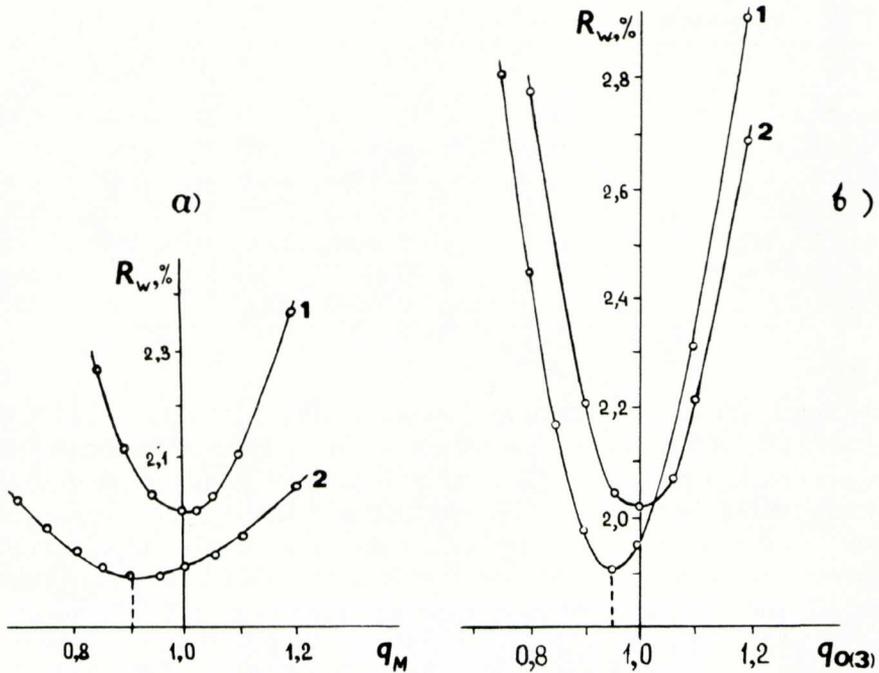


Fig. 1. The dependence $R_{wmin} = f(q_M)$ (a) and $R_{wmin} = f(q_{O(3)})$ constructed using step-by-step scanning for Ge- (1) and Ti-sillenites (2).

her words, the analysis of the R_{wmin} sections suggests a strict stoichiometry of the composition of the sample and permits one to write its formula as $Bi_{12}GeO_{20}$. Our above mentioned X-ray structural study of Ge-sillenite⁴ confirmed the neutron diffraction results and conclusions about the absence of vacancies in Ge-sublattice. Step-by-step scanning method makes it possible to choose $q_{Ge} = 1.00(5)$ ($B_{Ge} = 0.43(2) \text{ \AA}^2$). Thus, the information about $Bi_{12}GeO_{20}$ crystal being Ge atom defective⁶ was not confirmed.

The results for Ti-sillenite were different. In this case the minima of R_w functional have the values of q lower than unity both for Ti and O(3) atoms (curves 2 in Fig. 1 a, b). The neutron scattering length of Ti atoms is less than that of O atoms, that influences the accuracy of the determination of q values. For Ti, the range of minimum values of R_w is broader: minimum values of R_w functional extends from $q_{Ti} = 0.85$ to $q_{Ti} = 1.00$ (Fig. 1a, curve 1). In the case of O(3) atoms the minimum of the functional R_w is sharper- the confidence interval of $q_{O(3)}$ values is narrower. From curve R_w one can estimate the O(3) site occupancy $q_{O(3)} = 0.95(3)$. According to

electroneutrality principle the Ti site occupancy being equal to 0.90 should correspond to such amount of oxygen, that agrees with the value independently determined from curve 2 Fig. 1a. Another proof of this are reasonable values of thermal parameters of $B_{\text{Ti}} = 0.41(9)$ and $B_{\text{O}(3)} = 1.03(2) \text{ \AA}^2$. On the average, there are two oxygen vacancies per one Ti-vacancy. Thus, the chemical formula of Ti-sillenite should be written down as $\text{Bi}_{12} \text{Ti}_{0.90} \text{O}_{19.80}$. The appropriate atomic parameters are listed in Tables 2 and 3. The interatomic distances in Bi-polyhedra are compared in Table 4.

A comparison of results of the structural studies of Ge- and Ti-sillenites shows that the valence and size of Ge^{4+} -ion are optimum for constructing an ideal sillenite-type structure. The presence of a Ti^{4+} -ion in the structure of Ti-sillenite whose size significantly exceeds the optimum one gives rise to certain stresses within the structure, that are removed due to defective M tetrahedra. Let us consider the main structural peculiarities of

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) in Ge- and Ti-sillenites.

Atom	M Parameters	Ge	Ti
Bi	q	1.00	1.00
	x	0.17583 (5)	0.17647 (4)
	y	0.31845 (5)	0.31874 (4)
	z	0.01593 (5)	0.01544 (4)
	B	0.68 (1)	0.57 (1)
M	q	1.00	0.90 (8)
	$x = y = z$	0	0
	B	0.51 (2)	0.41 (9)
O(1)	q	1.00	1.00
	x	0.13478 (8)	0.13451 (6)
	y	0.25127 (8)	0.25032 (6)
	z	0.48587 (8)	0.48666 (6)
	B	0.86 (1)	0.74 (1)
O(2)	q	1.00	1.00
	$x = y = z$	0.19434 (9)	0.19217 (7)
	B	0.82 (2)	0.81 (2)
O(3)	q	1.00	0.95 (3)
	$x = y = z$	0.89968 (9)	0.89636 (7)
	B	1.10 (2)	1.03 (2)

Table 3. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) in sillenites with 'complex' M cations.

Atom	M	(Fe, P)	(Bi, Ga)	(Bi, Fe)	(Bi, Zn)	(Bi, V)
	Parameters					
Bi	q	1.00	1.00	1.00	1.00	1.00
	x	0.17680 (6)	0.17613 (4)	0.17631 (4)	0.17655 (4)	0.17740 (5)
	y	0.31974 (6)	0.31772 (4)	0.31786 (4)	0.31821 (4)	0.32235 (5)
	z	0.01927 (6)	0.01386 (4)	0.01395 (4)	0.01379 (4)	0.02293 (5)
	B	0.91 (1)	1.15 (1)	1.13 (1)	1.42 (1)	1.00 (1)
M	q	P 0.59 (2) Fe 0.35 (2)	Ga 0.50 (1) Bi 0.50 (1)	Fe 0.50 (2) Bi 0.50 (2)	Zn 0.33 (3) Bi 0.67 (3)	V 0.89 (1) Bi 0.03 (1)
	$x = y = z$	0	Ga 0 Bi -0.018(2)	Fe 0 Bi -0.018(2)	Zn 0 Bi -0.020(1)	0
	B	0.55 (3)	Ga 0.61 (3) Bi 0.88 (9)	Fe 0.64 (3) Bi 1.25 (13)	Zn 0.89 (7) Bi 0.88 (8)	0.6
	q	1.00	1.00	1.00	1.00	1.00
	x	0.1344 (1)	0.13526 (6)	0.13495 (7)	0.13539 (7)	0.13383 (8)
O(1)	y	0.2512 (1)	0.25192 (6)	0.25148 (7)	0.25132 (7)	0.24748 (8)
	z	0.4883 (1)	0.48552 (6)	0.48589 (7)	0.48631 (7)	0.49057 (8)
	B	0.98 (1)	1.09 (1)	1.11 (1)	1.20 (1)	1.13 (1)
	q	1.00	1.00	1.00	1.00	1.00
	$x = y = z$	0.1983 (1)	0.18964 (6)	0.18995 (7)	0.18757 (7)	0.20007 (8)
O(2)	B	1.10 (3)	1.03 (1)	1.07 (2)	1.17 (2)	1.09 (2)
	q	O _P 0.59 O _{Fe} 0.41	0.88 (1)	0.87 (1)	0.83 (1)	1.00
	$x = y = z$	O _P 0.9129 O _{Fe} 0.8970(5)	0.89344 (7)	0.89288 (8)	0.88989 (8)	0.90282 (8)
	B	O _P 1.42 (7) O _{Fe} 1.43 (9)	1.35 (2)	1.39 (2)	1.39 (2)	1.68 (2)
	q	-	-	-	-	0.09 (1)
O(4)	x	-	-	-	-	0
	y	-	-	-	-	1/2
	z	-	-	-	-	0
	B	-	-	-	-	1.8 (4)

Table 4. Bond length (Å) in Bi-polyhedra.

M	Ge	(Fe, P)	(Bi, Ga)	(Bi, Fe)	(Bi, Zn)	(Bi, V)
Bond						
Bi-O(1a)	2.072 (1)	2.075 (1)	2.0676 (7)	2.0676(8)	2.0657 (8)	2.089 (1)
-O(1b)	2.221 (1)	2.208 (1)	2.2458 (7)	2.2434 (8)	2.2509 (8)	2.186 (1)
-O(1c)	2.622 (1)	2.612 (1)	2.6298 (7)	2.6230 (8)	2.6233 (8)	2.602 (1)
-O(2)	2.2146 (6)	2.2101 (7)	2.2190 (4)	2.2201 (5)	2.2219 (5)	2.2175 (7)
-O(3d)	2.6241 (8)	O _P 2.756 (1)	2.5747 (6)	2.5735 (7)	2.5634 (7)	2.742 (1)
		O _{Fe} 2.639 (9)				
-O(4)	-	-	-	-	-	2.5833 (5)

Symmetry codes: (a) $1/2-x, 1/2-y, -1/2+z$; (b) $y z x$; (c) $y 1-z -x$; (d) $1-x, 1-y, -1+z$.

sillenites with an example of $\text{Bi}_{12}\text{GeO}_{20}$, an ideal sillenite. The structure framework is built up of Bi-polyhedra connected via common edges to form dimers that link translationally identical $[\text{MO}(3)_4]$ tetrahedra (Fig. 2). Pairs of the dimers extended along unit cell edges confine the volume voids near the (6b) site (0, 1/2, 0). On the whole, the structure can be reconstructed if we take into account that each O(3) vertex of a M tetrahedron is common for three Bi-polyhedra symmetrical relative to the three-fold axis that belong to dimers parallel to *a*, *b* and *c* axes. Besides we must take into account the I-lattice centering. The coordination environment of Bi atom that is at a (24f) site includes five oxygen atoms O(1a), O(1b), O(2), O(1c) and O(3) (Fig. 2). These oxygen atoms lie at distances 2.07; 2 x 2.22; 2 x 2.62 Å from Bi atom. Roughly, we can assume that O(1b), O(1c), O(2) and O(3) atoms lie in the same plane, the shortest Bi-O(1a) bond is perpendicular to that plane. The Bi atom is shifted from this plane by 0.1 Å in the direction opposite to O(1a) atom. As admitted in,³ the construction of Bi atom polyhedron is completed to a distorted polyhedron by its lone $6s^2$ electron pair oriented in the direction opposite to O(1a) atom.

A good example of a sillenite in which equivalent sites are occupied by cations with quite different ionic radii is (Fe, P)-sillenite. The analysis of the absorption spectra of this compound¹² showed that practically all iron atoms have oxidation state 3+. According to³ the chemical formula of this compound was initially written as $\text{Bi}_{12}(\text{Fe}_{0.5}\text{P}_{0.5})\text{O}_{20}$.

The refinement of the structure with this composition led to $R_w = 2.00$ and $R = 2.00\%$. However, the level of residual density on difference nuclear density maps near the origin exceeded the background $|\Delta\rho| \leq 0.2 \text{ fm}/\text{Å}^3$ by a factor of 7, approximately. The refinement of the scattering length of M cation using step-by-step scanning allowed us to es-

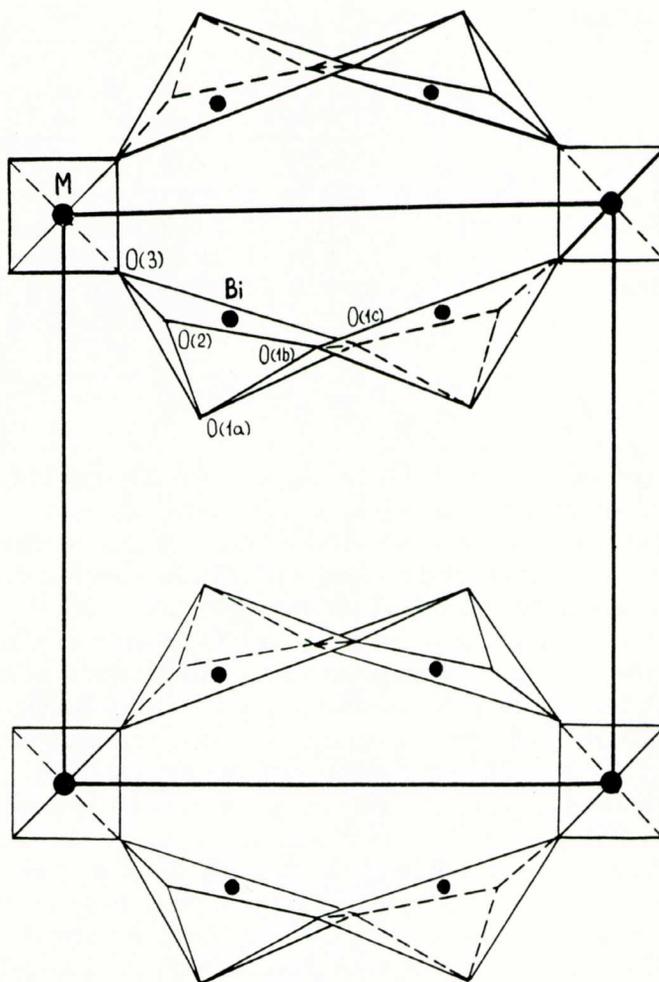


Fig. 2. A structure fragment of silenite type. Two dimers are shown, that relate translationally identical $[MO(3)_4]$ tetrahedra.

estimate its value as 6.41 (9), that corresponded to the composition $M = (Fe_{0.29}P_{0.71})$ and led to a lowering of R -factors down to $R_w = 1.75$ and $R = 1.82\%$. Besides, the level of residual density near $(0, 0, 0)$ site was reduced to background. The composition of the cation $M = P_x^{5+}Fe_y^{3+}$ can be found proceeding from two conditions. First, it was established that oxygen atoms in (Fe, P)-silenite fully occupy their sites and, consequently, the valence of M cations ($5x + 3y$) is equal to 4. The effective scattering length of M cation provides the second condition $5.13x + 9.54y =$

6.41. The solution of all these equations leads to the following composition of a statistical M cation: $(P_{0.59}^{5+} Fe_{0.36}^{3+} \square_{0.06})$. The error in the determination of cationic occupancy does not exceed 0.02.

The analysis of parameters of atomic thermal motion revealed that the large ($B = 1.94 \text{ \AA}^2$) ellipsoid of thermal motion of O(3) atom is extended along a strong chemical bond M-O(3) that contradicts the physical sense. The O(3) atom forms the tetrahedral environment of $M = (P, Fe)$ site and the elongated shape of its thermal motion ellipsoid is accounted for by statistical O(3) atom occupation of two sites corresponding to $[PO(3)_4]$ and $[FeO(3)_4]$ tetrahedra different in size. Strictly speaking, if M site is defective in cations, one could search for three different sites for the O(3) atom that would correspond to P-, Fe- and \square -tetrahedra. However, taking into account the low value of M cationic defectness (6%) we limited ourselves to a statistical division of O(3) atom site into two sites: $O_p(3)$ and $O_{Fe}(3)$. The occupancy of $O_p(3)$ site was fixed at a value equal to M site occupancy by P atoms, $q_{O_p(3)} = 0.59$. The value $q_{O_{Fe}(3)} = 0.41$ was chosen for $O_{Fe}(3)$ site, i.e. in this case we 'brought to coincidence' Fe- and \square -tetrahedra, because we supposed that the \square -O(3) distance is not less than the Fe-O_{Fe}(3) distance, due to near Bi atoms. The Fe-O_{Fe}(3) interatomic distances were determined using step-by-step scanning and equaled 1.814 Å, the P-O_p(3) distance being 1.534 Å. The compensation for different valence forces in Fe- and P-tetrahedra was made by varying distances in Bi-polyhedra (Fig. 3). The Fe³⁺ cation is larger in size and has a lower valence, the P⁵⁺ cation is smaller in size and has a higher valence as compared to the Ge⁴⁺ ion which is optimum for the sillenite structure. This causes a shortening of the Bi-O_{Fe} bond and an elongation of the Bi-O_p bond (Table 4), first of all, due to O(3) atom shifts (Fig. 3). Since M tetrahedra are

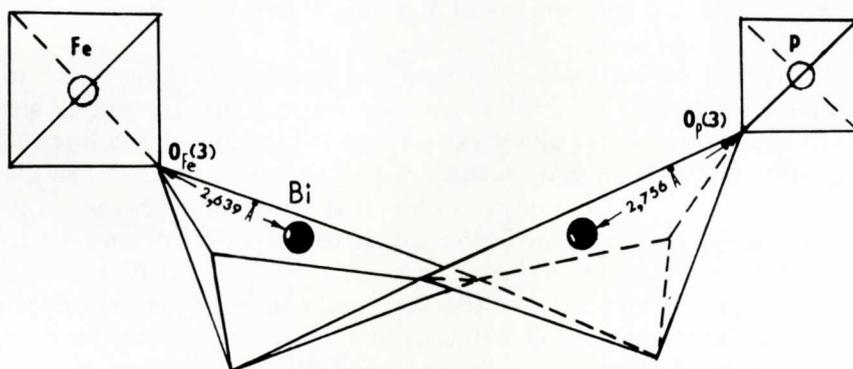


Fig. 3. Structure fragment of (Fe, P)-sillénite consisting of $[PO(3)_4]$ and $[FeO(3)_4]$ tetrahedra connected by a dimer of $[BiO_5]$ polyhedra.

occupied by Fe^{3+} and P^{5+} cations with different probabilities, there appear appropriate number of vacancies at M sites. The chemical formula of the sillenite studied is $\text{Bi}_{12}(\text{P}_{0.59}\text{Fe}_{0.35}\square_{0.06})\text{O}_{20}$.

Of special interest is the study of single crystals of (Bi, Ga)-, (Bi, Fe)- and (Bi, Zn)-sillenites. It is just on the basis of X-ray structural studies of sillenites with $\text{M} = (\text{Bi}, \text{Fe}), (\text{Bi}, \text{Zn})$ that the model of sillenite structure now accepted in the literature, was suggested.³ Besides, it was assumed that the ideal stoichiometry in the above compounds is achieved owing to Bi^{5+} cations occupying some tetrahedral sites. In accordance with the commonly used model the chemical formulae of the above sillenites were as follows: $\text{Bi}_{12}(\text{Bi}_{0.5}^{5+}\text{Ga}_{0.5}^{3+})\text{O}_{20}$, $\text{Bi}_{12}(\text{Bi}_{0.5}^{5+}\text{Fe}_{0.5}^{3+})\text{O}_{20}$, and $\text{Bi}_{12}(\text{Bi}_{0.67}^{5+}\text{Zn}_{0.33}^{2+})\text{O}_{20}$.

Our neutron diffraction studies have shown that the cationic relationship at M sites of these compounds is in conformity with those found before.³ However, the structures of these compounds exhibit some specific features that could not be explained within the framework of the commonly used sillenite model.

1. The structures are to a great extent O(3) atom defective. These O(3) atoms form the tetrahedral environment of M sites. For (Bi, Ga)-, (Bi, Fe)- and (Bi, Zn)-sillenites the O(3) occupancy factors are $q = 0.88$ (1), 0.87 (1) and 0.83 (1), respectively. Reliability of the determination of these values is confirmed by an essential lowering of R -factors, for instance, for (Bi, Zn)-sillenite from $R_w = 3.21$ to $R_w = 2.57\%$, as well as by comparatively low values of coefficients of the correlation between of q and B O(3) atoms, $A_{qB} = 0.80$.

2. Positive peaks 1.5, 1.3 and 2.5 $\text{fm}/\text{\AA}^3$ in height, respectively, were found on difference nuclear density maps of (Bi, Ga)-, (Bi, Fe)- and (Bi, Zn)-sillenites (Fig. 4). These peaks are positioned on three-fold symmetry axis in the direction towards the O(3) atoms, the distance between them and M (0, 0, 0) site being 0.5 \AA .

A detailed analysis of these specific features and checking of the appropriate models led to the following unambiguous structure model that provides an explanation of all the experimental observations. It follows directly from the O(3) atom occupancy factors that the effective valence of M cations is equal to 3+, but not to 5+ as it was assumed before. It follows from O(3) atom occupancy coefficients that, out of four oxygen atoms forming the tetrahedral environment of the M site only 3.5 are, in fact, present in the structures of (Bi, Ga)- and (Bi, Fe)-sillenites, for (Bi, Zn)-sillenite this value is 3.33. It means that one oxygen vertex is missing in a half of the M tetrahedra in (Bi, Ga)- and (Bi, Fe)-sillenites, there are 67% of such tetrahedra in (Bi, Zn)-sillenite. The number of defective tetrahedra in these compounds coincides with the independently determi-

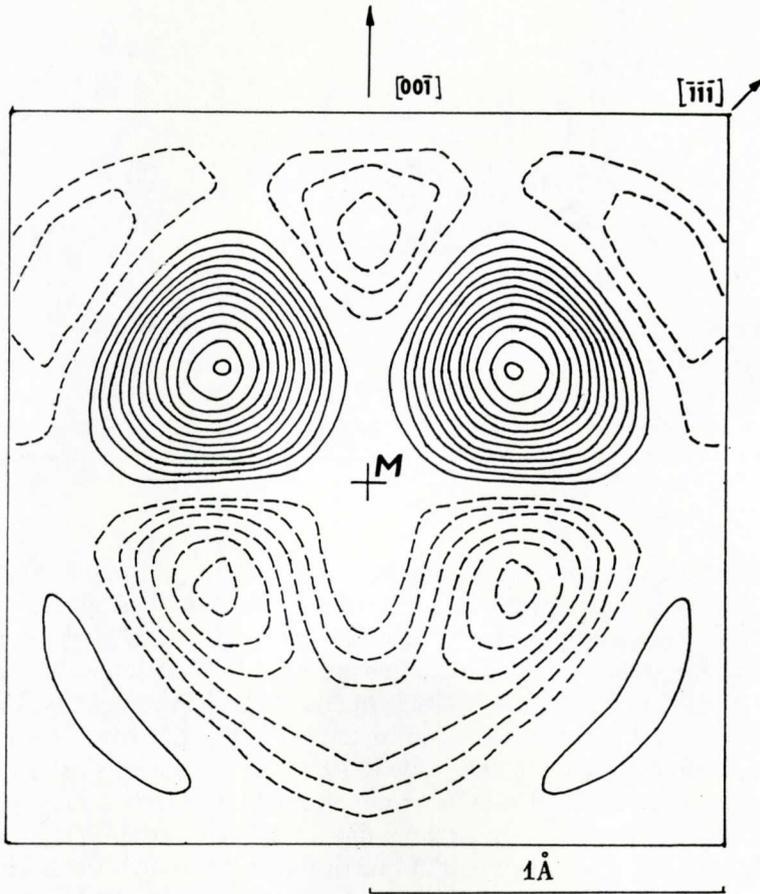


Fig. 4. $(1\ 1\ 0)$ section of difference nuclear density map in (Bi, Zn)-sillenite. Contours at $0.2\ \text{fm}/\text{\AA}^3$.

ned number of Bi atoms occupying the M sites. Thus, Ga, Fe or Zn atoms have a regular tetrahedral environment made up of O(3) atoms (Fig. 5a), M–O(3) distances being 1.879 (1), 1.890 (1) and 1.947 (2) Å, respectively, and they occupy 50% of the M sites in the (Bi, Ga)-, (Bi, Fe)- and (Bi, Zn)-sillenites. The Bi^{3+} cations in all these structures are positioned in tetrahedra with one missing vertex (Fig. 5b). This missing vertex provides space sufficient for hosting a lone $6s^2$ electron pair of Bi atom. The Bi atom located at M tetrahedral void is shifted from the origin towards the oxygen vacancy, that is evidenced by positive peaks on difference nuclear density maps (Fig. 4). Due to these shifts the $\text{Bi}_M\text{-O}$ interatomic distances increa-

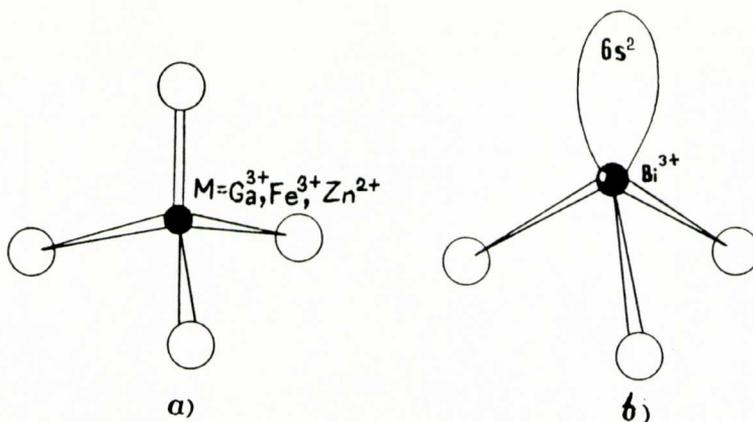


Fig. 5. Coordination arrangement of Ga, Fe, Zn (a) and Bi_M (b) atoms in structures of (Bi, Ga)-, (Bi, Fe)- and (Bi, Zn)-sillenites.

se, exceeding the value acceptable for the Bi-O bond. In all the cases the coordinates of the displaced Bi_M atom were determined using step-by-step scanning. R -factors were lowered down from $R_w = 2.57$ to $R_w = 1.70\%$ for (Bi, Zn)-sillenite, the residual density was also reduced to background $|\Delta\rho| \leq 0.2 \text{ fm}/\text{\AA}^3$. In the structure of (Bi, Zn)-sillenite this displacement was 0.354 \AA , that led to $\text{Bi}_M\text{-O}(3)$ distances being $2.091(6) \text{ \AA}$ and $\text{O}(3)\text{-Bi}_M\text{-O}(3)$ angles being 98.99° . Due to O(3) atom deficiency, some Bi polyhedra occupying (24f) sites, are four-pointed figures, their idealized geometry can be regarded as a trigonal dipyramid with axial O(1c) and O(2) bonds, and a lone electron pair at one of the equatorial vertices. There are at least two types of Bi-dimers in such structures (Fig. 6). The main rearrangements of the valence forces first of all, refer to dimers consisting of defective Bi(3)-polyhedra and related to them Bi(4)-polyhedra linked with the M tetrahedra that are occupied by cations with valences less than 4+ (Fig. 6). Changes in bond lengths in the above structures cause changes in the geometry of an 'averaged' Bi-polyhedron as compared to a Bi-polyhedron of an ideal sillenite $\text{Bi}_{12}\text{GeO}_{20}$. For example, the Bi-O(3) bond length in (Bi, Ga)-, (Bi, Fe)- and (Bi, Zn)-sillenites is $0.05 - 0.06 \text{ \AA}$ shorter than a similar bond in $\text{Bi}_{12}\text{GeO}_{20}$ (Table 4). The chemical formulae of the studied compounds should be written down as $\text{Bi}_{12}(\text{Bi}_{0.50}^{3+}\text{Ga}_{0.50}^{3+})\text{O}_{19.50}$, $\text{Bi}_{12}(\text{Bi}_{0.50}^{3+}\text{Fe}_{0.50}^{3+})\text{O}_{19.50}$ and $\text{Bi}_{12}(\text{Bi}_{0.67}^{3+}\text{Zn}_{0.33}^{2+})\text{O}_{19.33}$.

The main result of our study consists in the fact that a possibility of existence of sillenite structures with M cations having effective valences lower than 4 has been proved. It has also been proved that the valence of Bi atoms partially occupying the M sites is equal to 3. The possibility for Bi^{3+}

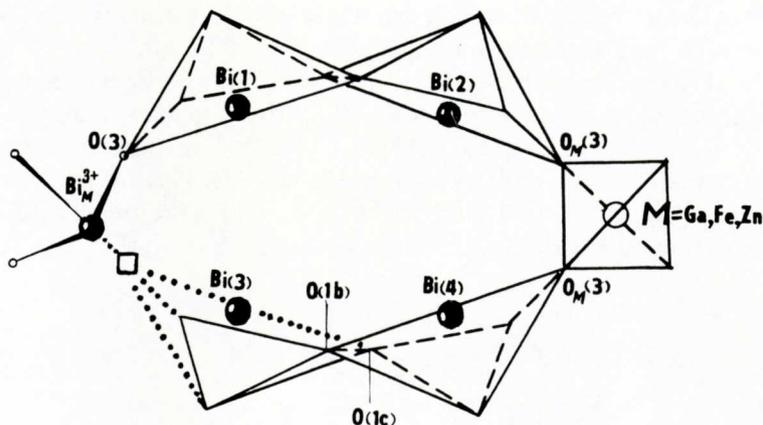


Fig. 6. A fragment of the sillenite structure.

cations to occupy M voids of the structure is ensured by oxygen vacancies appearing at certain crystallographic sites.

The studies of (Bi, V)–sillenite present interest because in this case the contradictions between the commonly use model for sillenites and the experimentally obtained physico-chemical characteristics are most vivid. The chemical formulae of this sillenite was initially reported to be $\text{Bi}_{12}(\text{Bi}_{0.5}\text{V}_{0.5})\text{O}_{20}$. For example, we would like to state an essential discrepancy between $D_m = 8.89 \text{ g cm}^{-3}$ and $D_x = 9.13 \text{ g cm}^{-3}$ of the single crystal.

After the structural model, corresponding to a composition $\text{Bi}_{12}(\text{Bi}_{0.5}\text{V}_{0.5})\text{O}_{20}$ was refined, the minimum R -factor was $R_w = 10\%$, the thermal parameter of the M cation had a physically meaningless anomalously high value $B_M = 10 \text{ \AA}^2$. The difference nuclear density maps contained a powerful negative peak of residual density at (0, 0, 0) site, exceeding the background $|\Delta\rho| \leq 0.02 \text{ fm/\AA}^3$ by two orders of magnitude. Refinement of the model without account of the M cation leads to low R -factors $R_w = 2.27$ and $R = 2.04\%$. The height of a peak of residual nuclear density at M site (0, 0, 0) $\rho = -0.03 \text{ fm/\AA}^3$ slightly exceeds the background. It means that the tetrahedral void contains both Bi atoms having a positive scattering length and V atoms, scattering in the counterphase, in a ratio ensuring approximately zero total scattering. When the tetrahedral site is fully occupied by Bi or V atoms the nuclear density maps constructed using F -calculated, contain peaks 73.9 and -1.5 fm/\AA^3 in height, respectively. A comparison of these values with the observed density suggests that this site is occupied mainly by vanadium. Since the scattering length of the M cation was close to zero, we could not determine reliably the value of the thermal parameter of this cation. It was specified as $B_M = 0.6 \text{ \AA}^2$, typical of other

sillenites. The effective scattering length or the M cation was estimated using step-by-step scanning and equaled $b_M = -0.07$ fm.

The difference residual density maps of (Bi, V)-sillenite possessed a specific feature that was not encountered in other sillenites, that is, a compact peak $2.3 \text{ fm}/\text{\AA}^3$ in height at (6*b*) site (0,1/2,0). The (6*b*) site is positioned at a centre of a void built by two dimers (Fig. 7). The distance between this site and the nearest Bi atoms is 2.58 \AA , while the neighbouring O atoms are situated at a distance not less than 2.88 \AA from that site. The re-

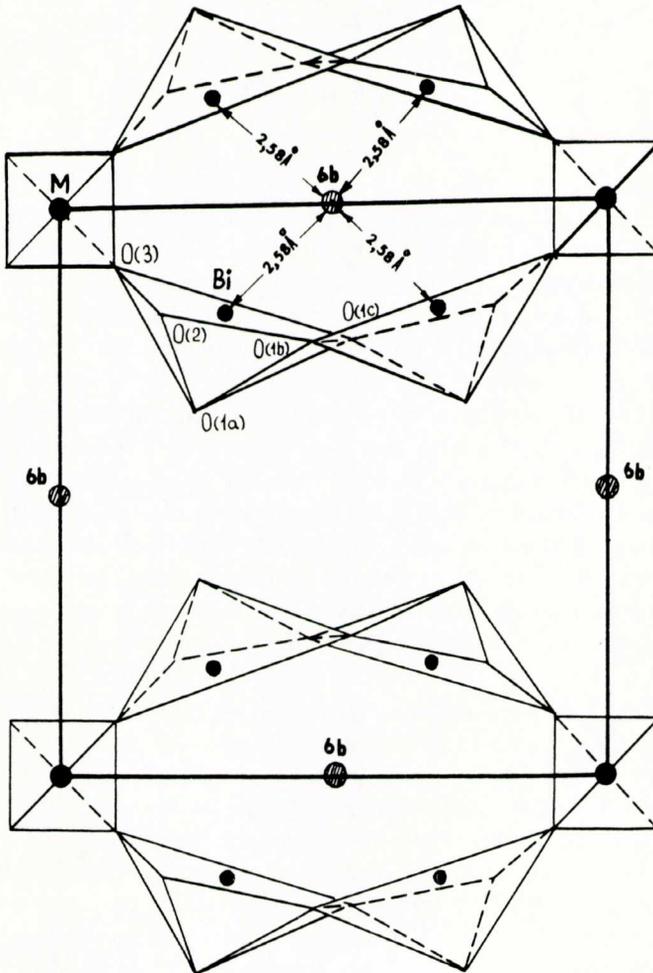


Fig. 7. The (6*b*) site in the sillenite structure. The distances between this site and nearest four Bi atoms are shown.

sidual nuclear density at the (6*b*) site should be naturally, attributed to an extra oxygen atom O(4). The presence of the extra O(4) atoms in the structure compensates for the M site occupation by V^{5+} ions. The refinement of this more complex model leads to the solution $q_{O(4)} = 0.09$ (1), $B_{O(4)} = 1.8(4) \text{ \AA}^2$, $R_w = 1.69$ and $R = 1.52\%$. The difference maps in this case become practically clear. The chemical formula of the compound should be written as $Bi_{12}MO_{20.27}$. The number of oxygen atoms and the scattering length of M cation determined from the diffraction data (taking into account the Bi_m and V valences as 5+ and 3+, respectively) suggested the following chemical formula $Bi_{12}(V_{0.89}Bi_{0.03}\square_{0.08})O_{20.27}$. Crystal density, calculated from our structural model $D_X = 8.91 \text{ g cm}^{-3}$ is in good agreement with $D_m = 8.89 \text{ g cm}^{-3}$. The presence of O(4) atoms in the structure results in a change of the coordinational arrangement of four nearest Bi atoms, that cease to be linked to O(3) atoms and become connected to the O(4) atom. Like in the case of an ideal Bi-polyhedron, the lone $6s^2$ electron pair of Bi atom oriented opposite the axial Bi–O(1*b*) bond completes the polyhedron to a distorted octahedron (Fig. 8). Four Bi-polyhedra sharing the O(4) atom vertex and linked in pairs by common faces form a peculiar cluster in the structure of (Bi, V)–sillenite (Fig. 8).

It should be emphasized that there can exist stable sillenite structures with M cations having effective valences larger than 4.

Thus, our neutron diffraction studies of single sillenite crystals confirmed that the model suggested in³ for these compounds needs revision.

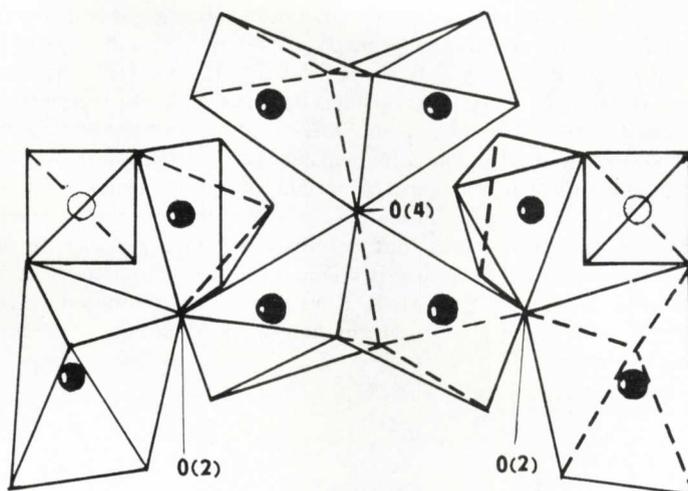


Fig. 8. Cluster of four Bi-polyhedra with an extra O(4) atom in the void of the structure of (Bi, V)–sillenite.

It has been proved that 1) the effective valence of M cations can be not only 4 exactly but also greater or smaller than 4+; 2) Bi atoms occupying the M site in some sillenites, are trivalent; 3) there can be not only 20 O atoms, but also more or less than 20 such atoms per a formula unit in sillenites. The flexibility and stability of sillenite structures with regard to M site occupancy by cations with different valences, sizes and electron structures is ensured by the following circumstance. The Bi atoms, whose polyhedra build up the framework, can have different coordination environments and they can change the geometry of coordination environment to a great extent. Our data permit one to predict new compositions of sillenites and their structure. Besides, these data provide information for establishing a correlation between the sillenite structure and physical properties.

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ABSTRACTS

Neutron and X-ray diffraction studies of sillenite single crystals $\text{Bi}_{12}\text{M}_x\text{O}_{20\pm\delta}$ with different M cations has been carried out. These investigations allowed us to establish the mechanism of isomorphous replacements and changes of atomic structure of these crystals. Realization of a particular mechanism depends on the type of M cation. The opinion that the effective valence of the M cation is rigorously equal to 4+, accepted in the literature, has been denied. It has been proved that the number of the O atoms per formula unit can be other than 20. We found that it is anionic sublattice of crystals that is responsible for a possible existence of a large family of isomorphic compounds, in this case. The formation of anionic vacancies at quite certain crystallographic sites or localization of additional anions at strictly determined places, within the structure ensure electroneutrality and stability of sillenite crystals with various types of M cations. Structure flexibility is attained due to mutual shifts of Bi and O atoms from the main sillenite framework, as well as due to orientational changes of a lone electron pair of Bi atom upon the formation of coordination polyhedra in a modified anionic sublattice.

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