

Atomic Structure and Crystal Chemistry of Sillenites: $\text{Bi}_{12}(\text{Bi}_{0.50}^{3+}\text{Fe}_{0.50}^{3+})\text{O}_{19.50}$ and $\text{Bi}_{12}(\text{Bi}_{0.67}^{3+}\text{Zn}_{0.33}^{2+})\text{O}_{19.33}$

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Abstract

The atomic structures of single crystals of the sillenites $\text{Bi}_{12}(\text{Bi}_{0.50}\text{Fe}_{0.50})\text{O}_{19.50}$ and $\text{Bi}_{12}(\text{Bi}_{0.67}\text{Zn}_{0.33})\text{O}_{19.33}$ have been determined at 293 K by neutron diffraction. Noticeable deviations from the ideal chemical formula $\text{Bi}_{12}\text{MO}_{20}$ have been found. $[\text{Fe}^{3+}\text{O}_4]$ or $[\text{Zn}^{2+}\text{O}_4]$ tetrahedra are replaced by umbrella-like $[\text{Bi}^{3+}\text{O}_3]$ groups statistically oriented with respect to the threefold axes of a cubic cell. A previous supposition concerning the presence of Bi^{5+} cations in M tetrahedra is not confirmed. $\text{Bi}_{12}(\text{Bi}_{0.50}^{3+}\text{Fe}_{0.50}^{3+})\text{O}_{19.50}$, $M_r = 2952.2$, cubic, $I23$, $a = 10.184(9) \text{ \AA}$, $V = 1056(3) \text{ \AA}^3$, $Z = 2$, $D_x = 9.28 \text{ g cm}^{-3}$, $\lambda = 1.167 \text{ \AA}$, $\mu = 0.002 \text{ cm}^{-1}$, $F(000) = 449.08 \text{ fm}$, final $R = 0.017$, $wR = 0.019$ for 375 unique reflections. $\text{Bi}_{12}(\text{Bi}_{0.67}^{3+}\text{Zn}_{0.33}^{2+})\text{O}_{19.33}$, $M_r = 2978.2$, cubic, $I23$, $a = 10.207(3) \text{ \AA}$, $V = 1063.4(9) \text{ \AA}^3$, $Z = 2$, $D_x = 9.30 \text{ g cm}^{-3}$, $\lambda = 1.167 \text{ \AA}$, $\mu = 0.0007 \text{ cm}^{-1}$, $F(000) = 444.23 \text{ fm}$, final $R = 0.016$, $wR = 0.017$ for 354 unique reflections.

Introduction

Non-linear optical characteristics, piezoelectricity and other physical properties which are important in the practical applications of sillenites have led to interest in their atomic structure. The general chemical formula of this large crystal family, which comprises over 40 members, is usually expressed as $\text{Bi}_{12}\text{MO}_{20}$. Structural studies of sillenites with different cations $M = \text{Ge}, \text{Ti}, (\text{Fe}, \text{P}), (\text{Bi}, \text{Ga}), (\text{Bi}, \text{V})$ (Radaev, Muradyan, Kargin, Sarin, Rider & Simonov, 1989*a,b*; Radaev, Muradyan, Sarin, Kanepit, Yudin, Maryin & Simonov, 1989) prompted us to investigate their atomic structure by neutron diffraction. Neutron diffraction has made possible the discovery of new structural features for this crystal class and established crystal-chemical laws concerning structural changes, which depend on the size and electronic structure of the M cations. In order to compare the possibilities of using X-ray and neutron diffraction analyses as a means of studying these compounds we have carried out both neutron and accurate X-ray structural investigations of a $\text{Bi}_{12}\text{GeO}_{20}$ single crystal. The data reported below

were obtained using X-rays. All reflections within a hemisphere of reciprocal space with $(\sin\theta/\lambda) = 1.0 \text{ \AA}^{-1}$ were measured with an Enraf-Nonius CAD-4F diffractometer, the errors in measurements of integrated intensities were less than 2%. Corrections were made for absorption and thermal diffuse scattering. The absolute configuration of the structure was reliably determined, the final R factors were $wR = 0.016$ and $R = 0.018$. Nevertheless, the presence of a large number of very heavy Bi atoms ($Z = 83$) considerably lowers the reliability of any determination of such parameters as crystallographic site occupancy by M cations and makes determination of this parameter for oxygen practically impossible. In this case the discrepancy factors are not sensitive to variations in O-atom site occupancies within the range $q = 0.70-1.20$. For the above q values the parameter B varies from 0.41 to 1.72 \AA^2 owing to a small contribution from O atoms and a strong correlation between the occupancy q and the thermal parameters B . In addition, severe X-ray absorption by sillenite crystals introduces considerable difficulties, *i.e.* some structural features which are reliably determined by neutron diffraction would be missed in X-ray studies. For instance, during the neutron diffraction study of (Bi,V) sillenite, *i.e.* $M = (\text{Bi}, \text{V})$, we found that the $(\frac{1}{2}, 0, 0)$ site, which is usually vacant in a sillenite structure, has a 9% oxygen occupancy. If this compound were to be studied by X-ray techniques such a small amount of oxygen would not be recognized in the difference electron density maps, since the level of residual density hardly exceeds the background. The use of neutron diffraction in studies of (Bi,V) sillenite ensured reliable localization of additional oxygen at the $(\frac{1}{2}, 0, 0)$ site and yielded the formula $\text{Bi}_{12}(\text{Bi}_{0.03}^{3+}\text{V}_{0.89}^{5+}\square_{0.08})\text{O}_{20.27}$. The level of residual nuclear density at the $(\frac{1}{2}, 0, 0)$ site exceeds the background by a factor of about 11. Allowance for this oxygen during refinement of the structure reduced the discrepancy factor from $wR = 0.023$ to $wR = 0.017$. It should be noted that the presence of additional oxygen in the structure of (Bi,V) sillenite is the result of an almost full occupancy of the M site by pentavalent vanadium.

Table 1. *Experimental and refinement details*

	Sillenites	
	(Bi,Fe)	(Bi,Zn)
Neutron source	VVRC reactor	
Monochromator	Cu(111), reflection geometry	
Wavelength (Å)	1.167	
Temperature (K)	293	
Crystal habit	Sphere	
Dimensions (mm)	5.7	5.1
Space group	I23	
Cell parameter (Å)	10.184 (9)	10.207 (3)
Reciprocal space	+h, ±k, ±l	
hkl range	h 0 → 16, k -16 → 16, l -16 → 16	
Scan mode	θ/2θ	
Intensity standards	One	
Decomposition (%)	< 3	
Reflections measured	3836	3527
Unique reflections [<i>I</i> > 3σ(<i>I</i>)]	3794	3473
Agreement factor on <i>I</i> , <i>R</i> _{int}	0.045	0.039
Reflections used	375	354
(sinθ/λ) _{max} (Å ⁻¹)	0.79	
Linear absorption coefficient (cm ⁻¹)	0.002	0.0007
<i>g</i> [*]	0.125 × 10 ⁻⁶	0.140 × 10 ⁻⁶
<i>R</i>	0.0173	0.0161
<i>wR</i>	0.0187	0.0170

* Isotropic extinction correction, Becker & Coppens formalism, type-I Lorentzian distribution.

All the previous investigations of sillenite single crystals since the initial study by Abrahams, Jamieson & Bernstein (1967) were carried out using X-ray analysis and were based on the oxygen-stoichiometry approach (Craig & Stephenson, 1975; Abrahams, Bernstein & Svensson, 1979; Svensson, Abrahams & Bernstein, 1979; Efendiev, Kulieva, Lomonov, Chiragov, Grandolfo & Veccia, 1981; Swindells & Gonzalez, 1988). It is this approach that led Craig & Stephenson (1975), who studied the structure of sillenites with *M* = (Bi,Fe) and *M* = (Bi,Zn), to a structural-model concept in which the *M*-cation valence or effective valence of the isomorphous cationic mixture at the *M* site is always equal to four. This means that the Bi atom partially occupying the *M* sites is pentavalent. However, it has not been proved experimentally that Bi⁵⁺ ions are present in the sillenite crystals. According to Craig & Stephenson (1975) strong support for their model comes from the fact that "the Bi³⁺ ion is too large and too asymmetric" to occupy the *M* sites in the structure. The chemical formulae Bi₁₂(Bi_{1/2}⁵⁺Fe_{1/2}³⁺)O₂₀ and Bi₁₂(Bi_{2/3}⁵⁺Zn_{1/3}²⁺)O₂₀ were suggested for the crystals studied and an assumption was made that the suggested structural model describes all the structural types of sillenites with various isomorphous mixtures at the *M* site. In particular, the formula Bi₁₂(Bi_{1/2}⁵⁺Bi_{1/2}³⁺)O₂₀ was suggested for the γ phase of Bi₂O₃.

Our neutron diffraction study of (Bi,Ga) sillenite, Bi₁₂(Bi_{0.50}³⁺Ga_{0.50}³⁺)O_{19.50} (Radaev *et al.*, 1989a), showed that the above model for this compound should be revised. We found that Bi atoms located at *M* positions in this sillenite are trivalent. Thus, it has been

proved that sillenites exist with *M* cations whose effective valence is less than 4+. The presence of a large and asymmetric Bi³⁺ cation with a lone electron pair in the tetrahedral voids arises from loss of one oxygen vertex in those tetrahedra which are populated by Bi atoms. Our results suggest that a similar structural model exists for both (Bi,Fe) and (Bi,Zn) sillenites. The results presented below confirm this assumption.

Experimental

The samples were grown by the Czochralski method. Neutron diffraction data for (Bi,Fe) and (Bi,Zn) sillenites were obtained on a Syntex P1 diffractometer. Analysis of the systematic absences and a subsequent averaging of symmetry-equivalent reflections confirmed the space group *I*23. The neutron diffraction experiment was carried out under the conditions given in Table 1.* Cell parameters were determined by least-squares refinement using 15 reflections with 69 < 2θ < 82°. The atomic neutron-scattering lengths were *b*_{Bi} = 8.5256 (14), *b*_{Fe} = 9.54 (6), *b*_{Zn} = 5.680 (5), *b*_O = 5.805 (4) fm.

(Bi,Fe) sillenite

All calculations were made according to the *PRO-METHEUS* program system (Zucker, Perenthaler, Kuhs, Bachman & Schulz, 1983) adapted for a NORD-500 computer (Muradyan, Sirota, Makarova & Simonov, 1985). Refinement of the standard structural model using anisotropic thermal parameters showed that the minimum *R* factors, *wR* = 0.027 and *R* = 0.023, correspond to equally probable population of the *M* site by Fe and Bi cations with *q*_{Fe} = *q*_{Bi} = 0.5. The value of the isotropic thermal parameter of this complex *M* cation is rather large, *B*_{*M*} = 1.86 (3) Å². Checking other atomic site occupancies revealed vacancies at the O(3) site. These O atoms form coordination tetrahedra with the *M* cations. The refined occupancy factor for the O(3) atom made it possible to reduce the *R* factors to *wR* = 0.023 and *R* = 0.021 at *q*_{O(3)} = 0.87 (1). The reliability of the *q*_{O(3)} value is confirmed by the rather low correlation coefficient between the occupancy and thermal parameter of the O(3) atoms *i.e.* *A*_{*qB*} = 0.81.

Analysis of the difference nuclear density maps revealed that the residual density considerably

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53347 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

exceeds the background only near the M site (0,0,0) (Fig. 1a). Positive peaks $1.3 \text{ fm } \text{\AA}^{-3}$ in height are located on the threefold axes at a distance of 0.56 \AA from the (0,0,0) site. A similar difference-density-distribution feature and a deficiency of O(3) atoms were found previously in our studies of single crystals of $\text{Bi}_{12}(\text{Bi}_{0.50}^{3+}\text{Ga}_{0.50}^{3+})\text{O}_{19.50}$. We believe that the model suggested and discussed in detail in Radaev *et al.* (1989a) is also correct in this case. The essence of the model is as follows. From the value $q_{\text{O}(3)} = 0.87$ it can be seen that there are 3.5 O(3) atoms per four vertices of an M tetrahedron in the structure. In other words, every other M tetrahedron lacks one oxygen vertex. The chemical formula is $\text{Bi}_{12}\text{MO}_{19.50}$ and it follows directly from valence balance that the M atom should be trivalent, *i.e.* $M = (\text{Bi}_{0.50}^{3+}\text{Fe}_{0.50}^{3+})$. Here Fe^{3+} cations are located in regular tetrahedra and positioned strictly at the origin (0,0,0), while Bi^{3+} cations are located in 'tetrahedra' with one vertex missing and displaced from the (0,0,0) site towards the oxygen vacancy, *i.e.* along the $[\bar{1}\bar{1}\bar{1}]$ direction. An equal probability of the loss of any of the four vertices in such a 'tetrahedron' statistically retains the cubic crystal symmetry.

It is impossible to determine the positional parameter x of the Bi_M atom occupying half of the tetrahedral voids by formally applying the least-squares technique because of a strong correlation between the x parameters of the Bi_M atom and the thermal parameters of the Bi_M and Fe atoms. A step-by-step scanning technique was used (Muradyan, Radaev & Simonov, 1989) in order to refine the structural model in this case. That is, for discrete values of the coordinate ($x = y = z$) of the Bi_M atom and within the range 0–0.03, a series of least-squares refinements of the other structural parameters were carried out. The minimum R factors, $wR = 0.019$ and $R = 0.017$, correspond to a shift of the Bi_M atom from the (0,0,0) site of 0.318 \AA . For such a model, difference nuclear density maps become practically clear – the level of residual density was reduced to the background value of $0.2 \text{ fm } \text{\AA}^{-3}$. The structural parameters of this model are listed in Table 2. Hence, this model agrees with all the observed features of the structure: the trivalent M cation, equally probable population of the tetrahedral M voids by Fe^{3+} and Bi^{3+} cations, as well as incomplete population of the sites by O(3) atoms.

The geometrical characteristics of the structure are listed in Table 3. The coordination polyhedron of the Fe atom is a regular tetrahedron with Fe–O distances $1.890 (1) \text{ \AA}$ (Fig. 2a). The Bi_M atom shifted from the (0,0,0) site by 0.318 \AA towards the oxygen vacancy is surrounded by three O(3) atoms at distances of $2.018 (8) \text{ \AA}$ so as to form an umbrella-like configuration $[\text{BiO}_3]$. The O– Bi_M –O angles are 99.7° . A lone $6s^2$ electron pair of this cation, pulled

towards the oxygen vacancy, completes the coordination polyhedron of Bi_M to form a tetrahedron (Fig 2b).

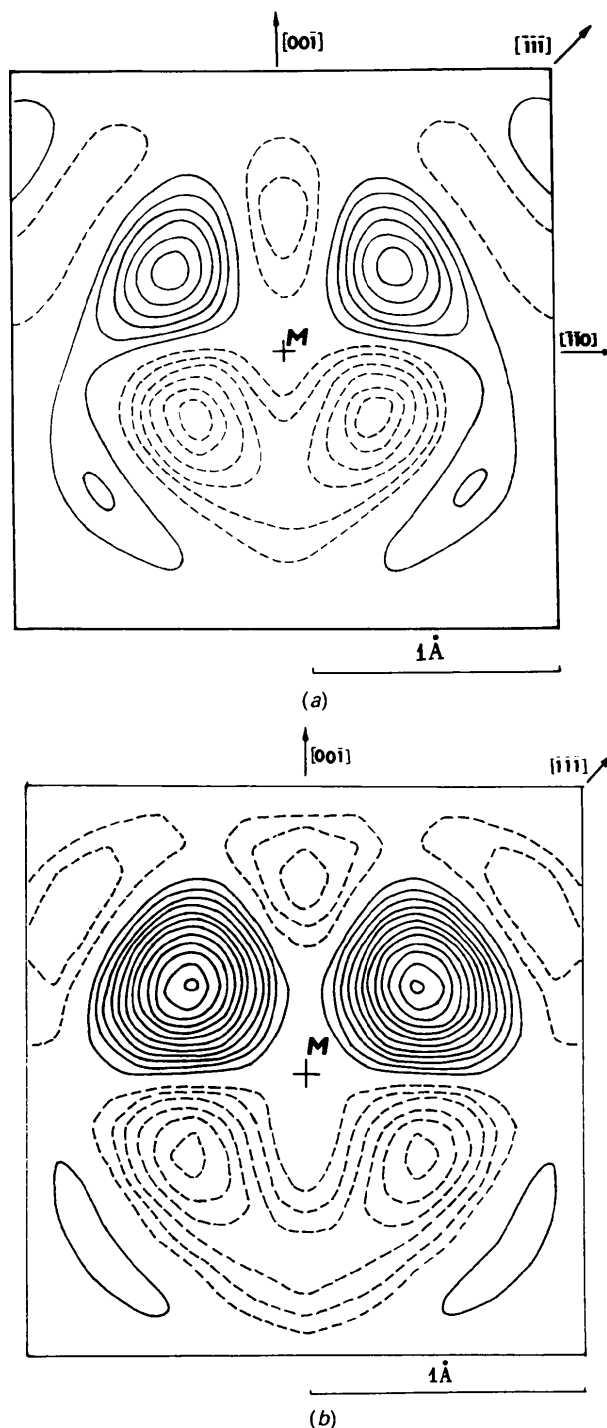


Fig. 1. Difference nuclear density maps in the (110) plane in (a) (Bi,Fe) silleenite and (b) (Bi,Zn) silleenite. Contour interval $0.2 \text{ fm } \text{\AA}^{-3}$. Negative contours dotted. The origin is denoted by a cross.

Table 2. Site-occupancy factors, fractional atomic coordinates and isotropic thermal parameters (\AA^2), with *e.s.d.*'s in parentheses

		Sillenites	
		(Bi,Fe)	(Bi,Zn)
Bi	<i>q</i>	1.00	1.00
	<i>x</i>	0.17631 (4)	0.17655 (4)
	<i>y</i>	0.31786 (4)	0.31821 (4)
	<i>z</i>	0.01395 (4)	0.13792 (4)
<i>M</i>	<i>B</i>	1.13 (1)	1.42 (1)
	<i>q</i>	Fe 0.50 (2)	Zn 0.33 (3)
		Bi 0.50 (2)	Bi 0.67 (3)
	<i>x = y = z</i>	Fe 0	Zn 0
O(1)	<i>q</i>	Bi -0.018 (2)	Bi -0.020 (1)
	<i>x</i>	Fe 0.64 (3)	Zn 0.89 (7)
	<i>y</i>	Bi 1.25 (13)	Bi 0.88 (3)
	<i>z</i>	1.00	1.00
O(2)	<i>q</i>	0.13495 (7)	0.13539 (7)
	<i>x</i>	0.25148 (7)	0.25132 (7)
	<i>y</i>	0.48589 (7)	0.48631 (7)
	<i>z</i>	1.11 (1)	1.20 (1)
O(3)	<i>q</i>	1.00	1.00
	<i>x = y = z</i>	0.18995 (7)	0.18757 (7)
	<i>B</i>	1.07 (2)	1.17 (2)
	<i>q</i>	0.87 (1)	0.83 (1)
O(3)	<i>x = y = z</i>	0.89288 (8)	0.88989 (8)
	<i>B</i>	1.39 (2)	1.39 (2)

(Bi,Zn) sillenite

Bi- and Zn-atom population analysis of the tetrahedral site confirmed the contents of the *M* cation (Bi_{0.67}Zn_{0.33}) as established by Craig & Stephenson (1975). The thermal parameter of this cation, 3.65 (8) \AA^2 , considerably exceeds those of other atoms within the structure. Refinement of the occupancy factor for the O(3) atom led to a considerable lowering of the *R* factors from $wR = 0.032$ to 0.026 [for $q_{O(3)} = 0.83$ (1)]. The correlation coefficient between the *q* and *B* parameters of this atom was comparatively small: $A_{qB} = 0.82$. No deviations from 1.00 (within experimental error) were observed for the occupancy coefficients of other atoms in the structure. Analysis of the difference nuclear density map revealed positive peaks 2.5 fm \AA^{-3} in height positioned on the threefold axes at a distance of 0.52 \AA from the origin (Fig. 1*b*). The described structural features of (Bi,Zn) sillenite, namely, a marked oxygen deficiency and the character of difference nuclear density maps, are in complete agreement with those found in (Bi,Fe) and (Bi,Ga) sillenites. Moreover, these features are most vivid in (Bi,Zn) sillenites. Thus, undoubtedly, the model for (Bi,Zn) sillenite suggested by Craig & Stephenson (1975) has to be revised. The value of the occupancy factor $q_{O(3)} = 0.83$ means that of the four O(3) atoms forming the tetrahedral coordination of the *M* cation only 3.33 are, in fact, present in the structure of (Bi,Zn) sillenite. In other words 67% of *M* tetrahedra in the structure lack one vertex. The number of such defect tetrahedra is equal to the independently determined number of Bi atoms which occupy 67% of the

Table 3. Interatomic distances in Bi polyhedra of (Bi,Fe) and (Bi,Zn) sillenites

The geometrical characteristics of a Bi polyhedron of an ideal sillenite Bi₁₂GeO₂₀ are given for comparison.

	Ge	Sillenites	
		(Bi,Fe)	(Bi,Zn)
Bi—O(1')	2.072 (1)	2.0675 (8)	2.0657 (8)
Bi—O(1'')	2.221 (1)	2.2434 (8)	2.2509 (8)
Bi—O(1''')	2.622 (1)	2.6230 (8)	2.6233 (8)
Bi—O(2)	2.2146 (6)	2.2201 (5)	2.2219 (5)
Bi—O(3'')	2.6241 (8)	2.5735 (7)	2.5634 (7)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) *y, z, x*; (iii) *y, 1 - z, -x*; (iv) $1 - x, 1 - y, -1 + z$.

tetrahedral positions. Thus the following structural model is realized for (Bi,Zn) sillenite: 33% of *M* sites are populated by Zn atoms having the regular tetrahedral environment of O atoms and with Zn—O distances 1.947 (2) \AA ; the remaining 67% of the tetrahedral voids host Bi atoms together with O atoms in an umbrella-like arrangement. It follows directly from the conditions of electroneutrality that Bi_{*M*} is trivalent. The chemical formula of (Bi,Zn) sillenite should be written as Bi₁₂(Bi_{0.67}³⁺Zn_{0.33}²⁺)O_{19.33}. Refinement of such a structural model leads to $wR = 0.017$ and $R = 0.016$, and the difference map becomes practically clear. Displacement of the Bi_{*M*} atom from the origin, as in the case of (Bi,Fe) sillenite, was determined by step-by-step scanning to be 0.354 \AA . The atomic parameters and geometrical characteristics of the structures studied are compared in Tables 2 and 3.

Discussion

According to the results of our neutron diffraction study trivalent Bi atoms occupy half the tetrahedral voids in the structure of (Bi,Fe) sillenite and two thirds of such voids in the structure of (Bi,Zn) sillenite. The possibility of a large and asymmetric Bi³⁺ cation occupying the tetrahedral voids of the structure is ensured by loss of one vertex in the appropriate number of *M* tetrahedra. The Bi³⁺ ion is displaced towards the oxygen vacancy, increasing the

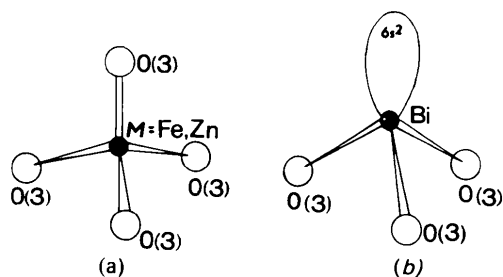


Fig. 2. Geometry of (a) Fe and Zn tetrahedra and (b) [BiO₃] umbrella-like groups in (Bi,Fe) and (Bi,Zn) sillenites.

distances between the Bi atom and the other three O(3) atoms up to allowed values. Bi—O distances in (Bi,Fe) sillenite are 2.018 (8) Å, while in (Bi,Zn) sillenite they are 2.091 (6) Å; valence angles are 99.7 and 98.9°, respectively. The space available to host the lone 6s² electron pair of the Bi atom is provided as a result of the oxygen vacancy. It should be noted that the value of the Bi_M displacement from the origin can be determined with greater reliability in (Bi,Zn) sillenite, since the number of Bi_M atoms and, consequently, the scattering ability of this cation, is greater than in (Bi,Fe) sillenite. Also, the difference between the scattering amplitudes of Bi and Zn is larger than for Bi and Fe.

The coordination polyhedron of the Bi atom occupying the 24(f) site in an ideal sillenite structure corresponds to a distorted tetragonal pyramid whose base is formed by the O(1ⁱⁱ), O(1ⁱⁱⁱ), O(2) and O(3) atoms, while the O(1ⁱ) atom occupies an axial vertex (Fig. 3a). Admittedly (Abrahams *et al.*, 1967; Craig & Stephenson, 1975), this Bi polyhedron is really an octahedron, the other position being occupied by its lone 6s² electron pair which is oriented in the direction opposite to the shortest Bi—O(1ⁱ) bond. Two Bi polyhedra sharing an O(1ⁱⁱ)—O(1ⁱⁱⁱ) edge form dimers (Fig. 4) which in turn form the framework of the sillenite structure. In the structures of (Bi,Fe) and (Bi,Zn) sillenites appropriate changes occur compared to an ideal Bi₁₂GeO₂₀ sillenite. Their structures contain at least three types of Bi polyhedra. The most important changes occur in the polyhedra which lack one O(3) vertex, shown as Biⁱ in Fig. 5. Such polyhedra constitute $\frac{1}{3}$ of all the Bi polyhedra in (Bi,Fe) sillenite and $\frac{1}{6}$ in (Bi,Zn) sillenite. The redistribution of valence forces in such polyhedra takes place, presumably, because of Bi displacement in the direction opposite to the O(3) atom vacancy. Orientation of a lone electron pair *E* changes in this case so as to make the new polyhedron stable (Fig. 3b). The shape of this new polyhedron corresponds to a distorted trigonal bipyramid with the equatorial plane containing E—O(1ⁱ)—O(1ⁱⁱⁱ) and the axial vertices along O(2) and O(1ⁱⁱ). Such a configuration is typical of 'molecules' of the AX₄E type. The second type of polyhedra which constitute half of all the Bi

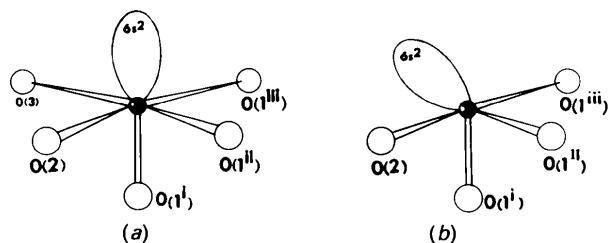


Fig. 3. Coordination of (a) Bi atoms of the main framework in an ideal sillenite and (b) Biⁱ atoms in (Bi,Fe) and (Bi,Zn) sillenites.

polyhedra in the structure of (Bi,Zn) sillenite and $\frac{3}{8}$ of those in (Bi,Fe) sillenite form a contact with O(3) atoms belonging to a [Bi_MO(3)₃] group. The configuration and valence forces in Biⁱⁱ polyhedra are close to those in an ideal sillenite Bi₁₂GeO₂₀. The third type of polyhedra, making up half of all Bi polyhedra in (Bi,Fe) sillenite and one third of those in (Bi,Zn) sillenite, form contacts with [Fe³⁺O(3)₄] and [Zn²⁺O(3)₄] tetrahedra, respectively. Such Bi polyhedra should differ from the Bi polyhedron which forms a contact with a quadrivalent cation polyhedron, [Ge⁴⁺O(3)₄] for instance. The local valence balance is regulated mainly by shortening of the Bi—O(3) bond length. Such structural changes are manifested in the change of geometry of an 'averaged' Bi polyhedron as compared with an ideal Bi

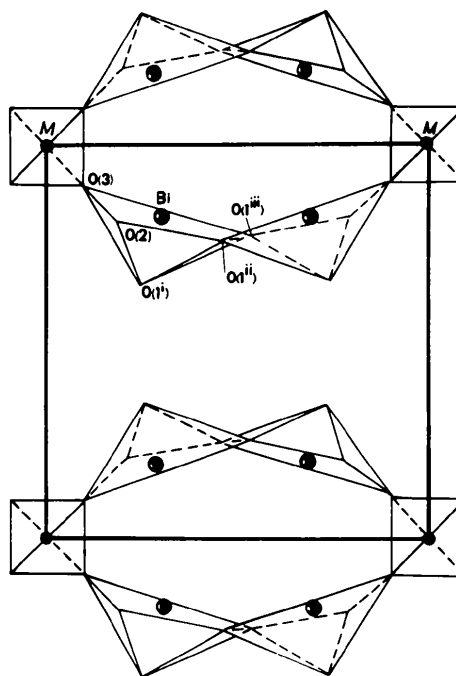


Fig. 4. A fragment of a sillenite-type structure. Two dimers which connect translationally identical [MO₄] tetrahedra are shown.

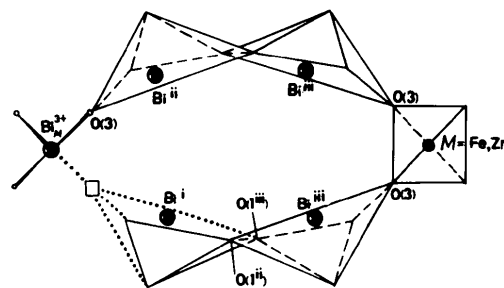


Fig. 5. Three types of Bi polyhedra in structures of (Bi,Fe) and (Bi,Zn) sillenites.

polyhedron in Bi₁₂GeO₂₀ (Table 3). The Bi—O(3) bond in (Bi,Fe) and (Bi,Zn) sillenites is 0.05–0.06 Å shorter than in Bi₁₂GeO₂₀, while the Bi—O(1ⁱⁱ) bonds are 0.02–0.03 Å longer than in Bi₁₂GeO₂₀. The stability of sillenite structures is ensured not only by changes in the anionic sublattice but also by shifts of the Bi atom itself. Bi-atom disordering with respect to a mean position is compensated for by a thermal parameter of the Bi atom whose thermal motion ellipsoid is extended along the O(3)—O(1ⁱⁱ) direction (Table 4). We see from Tables 3 and 4 that the structure distortions increase with larger oxygen O(3) losses as compared with an ideal sillenite Bi₁₂GeO₂₀.

From the new structural data obtained in our neutron diffraction study of (Bi,Ga), (Bi,Fe) and (Bi,Zn) sillenites we suggest an unambiguous structural model of the γ phase of Bi₂O₃, without the hypotheses concerning valence changes up to 5+ for Bi ions. In this model all the tetrahedral voids are occupied by Bi³⁺ cations in an umbrella-like arrangement, *i.e.* in each *M* tetrahedron one vertex is missing ($q_{O(3)} = \frac{3}{4}$). When all other anionic sites are fully occupied by O(1) and O(2) atoms there are 19 O atoms per formula unit. Anionic deficiency is compensated for by partial ($q = \frac{1}{6}$) occupancy of the 6(*b*) site (0, $\frac{1}{2}$, 0) by additional O(4) atoms, the total number of O atoms being 19.5 per formula unit. The 6(*b*) site is a void centre in the structure formed by two Bi dimers (Fig. 4). Population of this site by O atoms was confirmed by our studies of (Bi,V) sillenite. Equally probable vacancies in any of the four tetrahedral vertices and statistical occupation of one of the six possible 6(*b*) sites in the unit cell by O(4) atoms keep, on average, the crystal cubic symmetry and space group *I*23. The chemical formula of γ -Bi₂O₃ in this case will be Bi₁₂Bi³⁺O_{19.50} = Bi₂₄Bi₂³⁺O₃₉ = 13Bi₂O₃. This model explains an increased value in the lattice parameter $a = 10.268$ Å (Harwig, 1978) for γ -Bi₂O₃. We observed a similar increase in the lattice parameter in (Bi,V) sillenite resulting from partial occupation of an additional anionic site 6(*b*) by O(4) atoms.

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Table 4. Mean-square displacements (Å) of atoms during thermal motion in (Bi,Fe) and (Bi,Zn) sillenites

Similar atomic characteristics of an ideal Bi₁₂GeO₂₀ sillenite are given for comparison.

	Direction towards	Sillenites		
		Ge	(Bi,Fe)	(Bi,Zn)
Bi	O(1 ⁱ)	0.081	0.095	0.099
	O(1 ⁱⁱ)	0.099	0.148	0.174
	O(1 ⁱⁱⁱ)	0.100	0.125	0.139
	O(2)	0.095	0.109	0.116
	O(3 ^{iv})	0.100	0.151	0.177
O(1 ⁱ)	Bi	0.087	0.099	0.105
	Bi	0.090	0.102	0.105
	Bi	0.118	0.136	0.144
O(2)	Bi	0.086	0.094	0.096
	Bi	0.125	0.137	0.138

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