using only reflections with $\sin\theta/\lambda < 0.5$ Å^{-1}: the $P(NPCl_3)_3]^+$ cations obtained with data sets of increasing $\sin\theta/\lambda$ cut-offs revealed that above approximately 0.5 Å^{-1} the large number of weak reflections with relatively large experimental standard deviations leads to a disturbing increase in the noise level. The standard deviations (Coppens & Hamilton, 1968) do not include the errors of the scale factors and are larger near the atom centers (Stevens & Coppens, 1976). In compound (1) an additional phase error caused by the lack of a center of symmetry (Coppens, 1974) must be considered.

Despite the different crystallographic site symmetries of the cations in (1) and (2), the dynamic deformation density maps (see Fig. 7) show some common features: accumulation of negative charges between the atoms, charge transfer from the phosphorus to the more electronegative N atoms. Charge deficiency (positive charge) at the phosphorus atoms and higher charge densities along the P—N bonds than along the P—Cl single bonds were only observed in the deformation density maps of the centrosymmetric compound (2). Because of the mesomerism in the $[Cl—P(NPCl_3)_3]^+$ cations stated above and the small differences in the P—N bond distances, the charge densities along the P—N bonds of the $NPCl_3$ group are about the same or only slightly larger than the charge densities along the P—N bonds to the central phosphorus atom P(1).

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Structural Features of γ-Phase Bi_2O_3 and its Place in the Sillenite Family

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Abstract

A new atomic model of the γ-phase of bismuth trioxide, Bi_2O_3, has been suggested, explained and refined from powder neutron diffraction data. The data were collected at 293 K. $Bi_{12}Bi_{0.80}O_{19.20}$, $M_r = 2982.1$, cubic, $I23$, $a = 10.2501\ (5)$ Å, $V = 1076.9\ (2)$ Å^3, $Z = 2$, $D_m = 9.18$, $D_x = 9.20$ g cm^{-3}, $\lambda = 2.3145$ Å, $\mu = 0.0008$ cm^{-1}, $R_{wp} = 6.56\%$ for 1206 profile points. It was found that the tetrahedral sites

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in the structure are populated by Bi^{3+} ions with a probability of 80%. The O atoms which form the tetrahedral environment of these Bi atoms occupy their sites with the same probability. An expanded chemical formula of γ-Bi_2O_3 is written as $Bi_{12}Bi_{0.80}O_{19.20} \Longrightarrow Bi_{12}[BiO_3]_{0.8}[\square O_4]_{0.2}O_{16}$. There are umbrella-like $[BiO_3]$ groups and void tetrahedra instead of $[BiO_4]$ tetrahedra in the structure. Orientational disorder of the umbrella-like groups keeps the cubic symmetry of the crystal. The structure of γ-Bi_2O_3 exhibited regular changes as compared to the structure of the ideal sillenite $Bi_{12}GeO_{20}$ and the structures of previously investigated sillenites.

Introduction

The sillenite family $Bi_{12}MO_{20}$ (space group $I23$) now comprises over 40 members and is the subject of numerous research works. Undoubtedly, of major interest for mineralogists, crystal chemists and physicists is the structure of γ-phase Bi_2O_3, *i.e.* the mineral sillenite. Despite the fact that the γ-phase of Bi_2O_3 has been known for over 50 years (Sillen, 1937), data on its structure are insufficient. The high-temperature powder diffraction study of γ-Bi_2O_3 carried out by Harwig (1978) is the only structural study available. This study confirmed that γ-Bi_2O_3 is isostructural with sillenites. However, the low quality of the experimental data and impurities such as the δ-phase of Bi_2O_3 in the sample prevented Harwig (1978) from obtaining reliable structural data. The R factor was rather high (14%) and the author himself regarded his results as preliminary. The atomic structure of the γ-phase of Bi_2O_3 has been the subject of various investigations. According to Aurivillius & Sillen (1945), it is probable that the structure of γ-Bi_2O_3 is the same as that of $Bi_{12}SiO_{20}$ with vacancies in the oxygen lattice. However, Schumb & Rittner (1943) believed that isomorphous replacement of Si^{4+} by Bi^{3+} is unlikely because of the unfavorable size factor. Recently, some new proposals have appeared concerning the structure of γ-Bi_2O_3. Here we consider two of them which are based on the commonly used structural model of sillenites suggested by Craig & Stephenson (1975). These authors make use of the previously published X-ray structural data on sillenite structures containing M = Si and Ge cations (Abrahams, Bernstein & Svensson, 1979; Svensson, Abrahams & Bernstein, 1979) as well as the results of their own X-ray structural studies of crystals with M = (Bi,Fe) and (Bi,Zn). The model is based on the supposition that the anionic sublattice of sillenites has no defects. In such cases there are always exactly 20 oxygen atoms per formula unit in the crystal, and these atoms fully occupy their crystallographic sites. The effective valency of the M cation which can also be represented by isomorphous mixtures, should in this case be exactly equal to 4+. Craig & Stephenson (1975) paid special attention to the case where the M sites are partially occupied by Bi atoms. In the compounds they studied, the Bi_M atoms form an isomorphous mixture with cations whose valency is less than 4+. In order to fulfil the above conditions Craig & Stephenson (1975) naturally supposed that Bi atoms occupying the M sites are pentavalent. This hypothesis is consistent with tetrahedral coordination of the M sites by O atoms, since large Bi_M^{3+} cations with their $6s^2$ electron lone pair can hardly be located in regular tetrahedra.

Proceeding from this model, Craig & Stephenson (1975) suggested that the chemical formula of γ-Bi_2O_3 should be written as $Bi_{12}(Bi^{3+}_{1/2}Bi^{5+}_{1/2})O_{20}$, supposing that Bi^{5+} and Bi^{3+} ions statistically alternate over the tetrahedral sites. This hypothesis about the structure of γ-phase Bi_2O_3 is commonly accepted nowadays. However, in this case the Bi_M^{3+} ions should be located in the above-mentioned regular tetrahedra, and thus the problem of the arrangement of their electron lone pairs remains unsolved. Recently, another model of the structure of γ-Bi_2O_3 has been suggested on the basis of the same structural model of sillenites. The authors of this model (Watanabe, Kodama & Takenouchi, 1990) attempted to overcome the above difficulty by supposing that all M sites in the structure are fully occupied by pentavalent bismuth only, while there are appropriate Bi-atom vacancies at $24(f)$ sites to fulfil the condition of electroneutrality. The chemical formula γ-Bi_2O_3 in this case becomes $Bi^{3+}_{11.67}Bi^{5+}O_{20}$. The models of γ-Bi_2O_3 described above assume the presence of Bi_M^{5+} ions in the structure, which, in the opinion of Watanabe *et al.* (1990), is a 'bottleneck' of those structural models, because there is no experimental evidence for the presence of Bi^{5+} ions in γ-Bi_2O_3 crystals.

We have carried out neutron diffraction studies on some single sillenite crystals with various types of cations M (Radaev, Muradyan, Kargin, Sarin, Rider & Simonov, 1989*a*,*b*; Radaev, Muradyan, Sarin, Kanepit, Yudin, Mar'in & Simonov, 1989; Radaev, Muradyan & Simonov, 1990; Radaev, Muradyan, Simonov, Sarin, Rider, Kargin, Volkov & Skorikov, 1990). We found that several structural models exist for the sillenites *i.e.* there is no universal model for all the sillenites. Each particular model is unambiguously defined by the type of cation M. When the M sites are partially occupied by Bi atoms the valency of the latter is 3+ while the effective valency of an M cation is less than 4+ (Radaev *et al.*, 1989*a*; Radaev, Muradyan & Simonov, 1990). The distribution of Bi^{3+} ions over M sites is accompanied by an appropriate number of O-atom vacancies making up the coordination of these sites. Thus the structure keeps its electroneutrality and a space appears which is required for an electron lone pair (E) of the Bi_M atoms. The Bi atom itself is coordinated to three O atoms which together form an umbrella-like configuration $[\text{Bi}_M\text{O}_3E]$. When the effective valency of the M cation exceeds 4+ (Radaev, Muradyan, Sarin *et al.*, 1989) the electroneutrality of the structure is ensured due to the location of additional O atoms in some framework voids near the 6(b) sites ($\frac{1}{2}$,0,0).

Our novel structural data allowed us to suggest our own model of the structure of γ-phase Bi_2O_3 (Radaev, Muradyan & Simonov, 1990). In this model the presence of Bi^{5+} ions in the structure is not needed. According to this model, all the M sites in γ-Bi_2O_3 are occupied by trivalent Bi cations. The $[\text{Bi}_M\text{O}_3E]$ groups have an umbrella-like configuration and all the M tetrahedra have one O-atom vertex missing. The cubic symmetry of the structure is retained due to orientational disorder of these groups. To ensure the electroneutrality of the structure some of the framework voids located near the 6(b) sites are occupied by an appropriate number of additional O atoms. The extended chemical formula of γ-Bi_2O_3 is written in this case as $\text{Bi}_{12}^{3+}\text{Bi}^{3+}\text{O}_{19.50} = \text{Bi}_{26}\text{O}_{39} = 13\text{Bi}_2\text{O}_3$.

Thus, there are numerous hypotheses concerning the structure of γ-Bi_2O_3. However, the final solution to the problems of the atomic structure of γ-Bi_2O_3 can only be obtained experimentally.

Experimental

Bismuth(III) oxide of the 'highly pure 13.3' brand was used to prepare γ-Bi_2O_3. The reagent was $\geq$99.5% pure. 10 g of α-Bi_2O_3 powder containing 0.1 mass% of CdO, ground in advance in an agate mortar for 30 min, was placed in a platinum boat measuring 8 × 10 × 50 mm. The layer was 3–4 mm thick. The sample was heated to 1053 K in a resistance furnace, held at this temperature for 4 h, and then slowly cooled to 673 K at a rate of 1 K min^{-1}, before finally removing the sample from the furnace. The sample obtained was a rather hard yellow sinter, which was then crushed and ground carefully in the agate mortar. According to the X-ray phase-analysis data the sample corresponded fully to a sillenite X-ray diffraction pattern (Sillen, 1937) and consisted of a single phase. Differential thermal analysis (DTA) was carried out and thermogravimetric (TG) data for γ-Bi_2O_3 were measured on an STA-409 (Netrsch) thermoanalyzer in air in platinum anvils (Fig. 1). The DTA curve shows an exothermal effect due to phase transformation of metastable γ-Bi_2O_3 to stable α-Bi_2O_3 ($\Delta H_{\gamma\to\alpha} = 11.1\ \text{J g}^{-1}$). Upon further heating the phase underwent intrinsic $\alpha \to \delta$ (1003 K) transformations and melted (1098 K). No anomalies were found on the TG curve upon heating.

The diffraction data were collected at 295 K on a low-background multiple-detector DISK diffractometer mounted on an IR-8 reactor at the I. V. Kurchatov Institute of Atomic Energy. This instrument has been described by Glazkov, Naumov, Somenkov & Shilstein (1988). The atomic neutron-scattering lengths were: $b_{\text{Bi}} = 8.5256 \times 10^{-13}$ and $b_{\text{O}} = 5.805 \times 10^{-13}$ cm. The sample was placed in an open cylindrical vanadium container 5 mm in diameter and 50 mm high. The data were recorded at intervals of 0.09° 2θ over the angular range shown in Table 1.* A total of 1206 profile points were measured.

The full-profile analysis of the powder neutron diffraction pattern was carried out according to the Rietveld technique (Rietveld, 1969) using the program by Wiles & Young (1981). The background was approximated by a four-parameter polynomial in $(2\theta)^n$, where n had values between 0 and 3 and was refined simultaneously with the unit-cell parameter, zero-point, peak-width and asymmetry parameters, as well as the positional and isotropic thermal parameters of the atoms. The shape of the diffraction peaks was Gaussian. The variation of width with scattering angle 2θ is described by the formula $H = [U\tan^2\theta + V\tan\theta + W]^{1/2}$. At the final stage of refinement the maximum value of the shift of the parameters did not exceed 8% of the appropriate standard deviation. The experimental and refinement details are listed in Table 1. The experimental, calculated and difference neutron diffraction patterns of the γ-phase of Bi_2O_3 are shown in Fig. 2.

Results

The structural model suggested by Svensson *et al.* (1979) was used as the starting point for refinement.

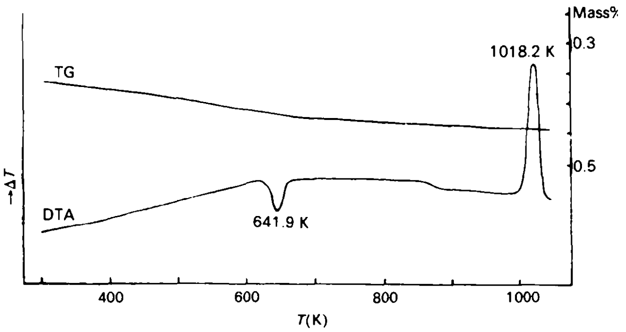

Fig. 1. The DTA and TG curves.

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* A list of powder neutron diffraction data has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55123 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0321]

Table 1. *Experimental and refinement details*

Wavelength (Å)	2.3145 (3)
Monochromator	C(002)*
Space group	*I*23
Cell parameter (Å)	10.2501 (5)
2θ scan range (°)	8 114
Max. step intensity	1 635 884
No. of unique reflections	49
No. of structural parameters†	15
No. of profile parameters	10
R_{wp} (%)‡	6.56
R_p (%)	4.78
R_B (%)	4.63
R_F (%)	3.40
R_{exp}	3.15

* Pyrolytic graphite.

† Includes atomic coordinates and isotropic thermal parameters, occupancy factors of Bi_M and O(3) atoms and unit-cell parameter.

‡ Weighting factor of y_i is from $w_i = (\sigma_i)^{-2}$.

Refinement of this model using the isotropic thermal approximation led to $R_{wp} = 6.73$, $R_p = 4.97$, $R_{exp} = 3.15$, $R_I = R_B = 5.24$ and $R_F = 4.09\%$. In this case the thermal parameters of Bi_M and O(3) atoms (the latter make up the tetrahedral environment of the *M* site) had anomalously large values of 5.4 (4) and 8.4 (4) Å^2, respectively. This could be due to deficiencies at the respective sites. At the next stage of step scanning, the site-occupancy coefficients of Bi_M and O(3) atoms were refined. We usually use this scanning technique (Muradyan, Radaev & Simonov, 1989) in order to refine strongly correlating parameters, *q* and *B* in this particular case, as well as for correct estimation of errors in the determination. A series of fixed values of a correlating parameter are chosen, then the whole structural model is refined for each value and the parameters corresponding to the minimum *R* factor (R_{wp} in our case) are determined.

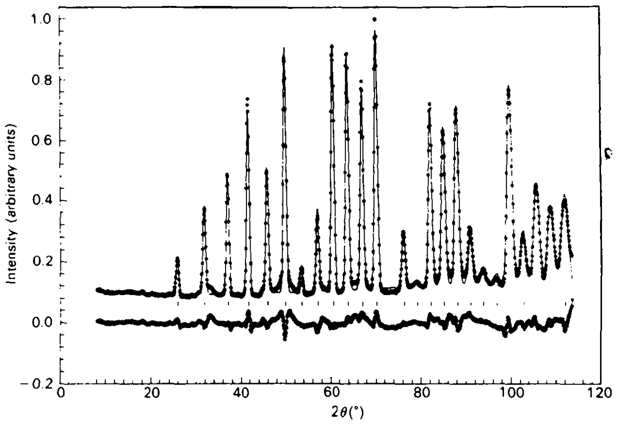


Fig. 2. Neutron diffraction patterns from γ-Bi_2O_3. Observed data are indicated by crosses and the calculated profile is the continuous line overlying them. The short vertical lines below the pattern represent the positions of all possible Bragg reflections. The lower curve is the difference between the observed and calculated intensity at each step plotted on the same scale.

Table 2. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2), *with e.s.d.'s in parentheses*

	x	*y*	*z*	*B*
Bi	0.1760 (5)	0.3203 (5)	0.0096 (5)	1.6 (1)
Bi_M	0	0	0	0.8 (4)
O(1)	0.1365 (8)	0.2476 (8)	0.5038 (8)	1.2 (1)
O(2)	0.1874 (8)	0.1874 (8)	0.1874 (8)	2.6 (2)
O(3)	0.8885 (8)	0.8885 (8)	0.8885 (8)	2.7 (4)

In order to choose the solution correctly in the region of minimum *R* factors, which has the appearance of a plateau for cases of strong correlation, some additional information should be included, for example, reasonable values of thermal parameters. The analysis of $R_{wp}(q_{Bi_M})$ and $R_{wp}[q_{O(3)}]$ dependences constructed in this manner showed that the acceptable solution $q_{Bi_M} = 0.83$ (5) and $q_{O(3)} = 0.76$ (9) corresponds to the middle of regions of minimum values of these functions and the lowest *R* factors (Table 1).

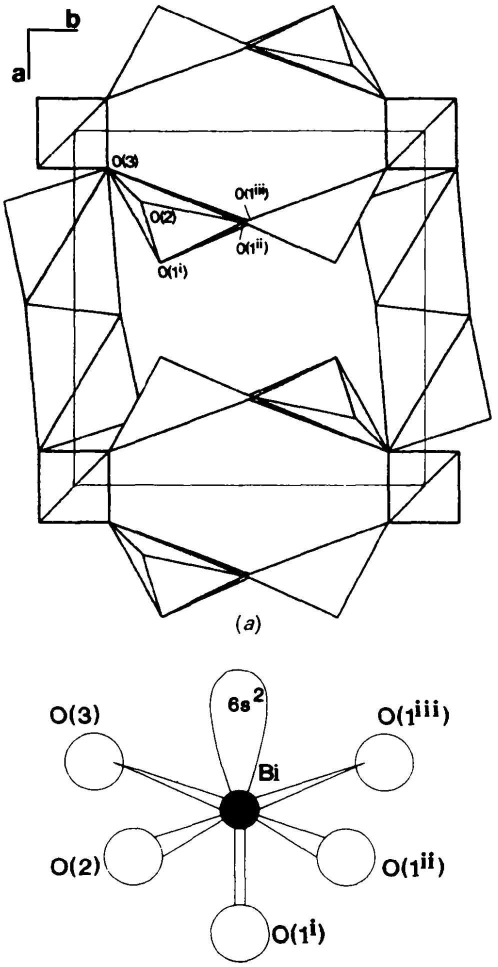
The results obtained lead to an unambiguous model that accounts for all the experimental data available. The essence of the model is as follows. (1) Bi_M^{3+} cations do not fully occupy the *M* site, they are coordinated to three of the O(3) atoms and together form umbrella-like $[Bi_MO(3)_3E]$ groups. (2) Vacant *M* sites have a tetrahedral environment made up of four O(3) atoms. The trivalent Bi_M cation and the Bi_M- and O(3)-atom deficiencies suggest the following equation – a condition of valency balance with regard to the unit cell – $72 + 3x = 64 + 2y$, where *x* and *y* are the number of Bi_M and O(3) atoms per unit cell. Then, if we suppose that all the vacancies of the O(3) atom are due only to the umbrella-like environment of the Bi_M^{3+} cation formed by O(3) atoms, we arrive at the equation: $y = 8 - x$. Solution of these two equations leads to the values $x = 1.6$ or $q_{Bi_M} = 0.08$, taking into account the multiplicity of the site and $y = 6.4$ or $q_{O(3)} = 0.08$. Comparison of these values with the data obtained by us shows that they coincide within the accuracy of our measurements. Therefore, in the final stage of the refinement we fixed the occupancy coefficients of the Bi_M and O(3) atoms as 0.8. The refined coordinates and atomic thermal-motion parameters of the accepted structural model are listed in Table 2. In the course of studies of (Bi,Ga), (Bi,Fe) and (Bi,Zn) sillenites (Radaev *et al.*, 1989*a*; Radaev, Muradyan & Simonov, 1990) whose structures also contain umbrella-like $[Bi_MO(3)_3E]$ groups, we found that the Bi_M atoms are displaced towards oxygen vacancies by 0.32–0.35 Å. The Bi_M—O(3) distances then increase, to acceptable values of 2.01–2.09 Å (Radaev *et al.*, 1989*a*; Radaev, Muradyan & Simonov, 1990). In the case of γ-Bi_2O_3, the mean *M*—O(3) distance within the structure was 1.980 (6) Å. We assume that in γ-Bi_2O_3 the Bi_M atoms are also displaced towards oxygen vacancies, but this displacement cannot be significant.

The suggestion made by Radaev, Muradyan & Simonov (1990) concerning partial occupancy of the 6(*b*) site by additional O atoms, was not, in fact, confirmed. The chemical formula of the γ-phase of Bi_2O_3 studied by us should be written as $Bi_{12}^{3+}Bi_{0.80}^{3+}O_{19.20} \Rightarrow Bi_{12}[BiO_3]_{0.8}[\square O_4]_{0.2}O_{16} \Rightarrow 6.4Bi_2O_3$.

Discussion

Our results show that, strictly speaking, none of the hypotheses made previously concerning the structure of γ-phase Bi_2O_3 (Craig & Stephenson, 1975; Watanabe *et al.*, 1990; Radaev, Muradyan & Simonov, 1990) have been confirmed. Our model (Radaev, Muradyan & Simonov, 1990) was only partially true, *i.e.* when we supposed that all Bi atoms in this compound are trivalent and all Bi_M^{3+} ions are coordinated to three O atoms together forming an umbrella-like $[Bi_MO_3E]$ arrangement.

It follows from the results of study that the specific features of γ-phase Bi_2O_3 as compared to the structure of an ideal $Bi_{12}GeO_{20}$ sillenite (Radaev, Muradyan, Simonov, Sarin *et al.*, 1990) (Fig. 3*a*) are Bi_M- and O(3)-atom deficiency. The Bi-atom polyhedron within the framework of an ideal $Bi_{12}GeO_{20}$ sillenite is a distorted tetragonal pyramid, whose equatorial plane is formed by $O(1^{ii})$, $O(1^{iii})$, O(2) and O(3) atoms, the $O(1^{i})$ atom being the axial vertex. The $6s^2$ electron lone pair makes this polyhedron a distorted octahedron (Fig. 3*b*). The cationic and anionic deficiency of the structure of γ-Bi_2O_3 results in redistribution of valence forces in the Bi polyhedra of the framework, which occurs due to mutual shifts of O and Bi atoms. The main atomic shifts take place in the equatorial plane of the Bi polyhedra and are accompanied by a change in the orientation of the electron lone pair (*E*) of the Bi atom. In the structure of γ-Bi_2O_3 the most remarkable redistributions of bond lengths occur in Bi polyhedra of the framework with one oxygen vertex missing. 20% of all the Bi polyhedra are such polyhedra in the structure of γ-Bi_2O_3. Their idealized geometry is a trigonal bipyramid with an electron lone pair in the equatorial plane E—$O(1^{i})$—$O(1^{ii})$ and axial vertices $O(1^{iii})$ and O(2). In these polyhedra there may be a substantial reduction of the long Bi—$O(1^{iii})$ bond and it becomes similar to another axial Bi—O(2) bond, which is elongated due to Bi-atom shifts. The second group of polyhedra in which significant redistribution of valence forces takes place are Bi polyhedra linked to void *M* tetrahedra. There are 20% such Bi polyhedra in the framework of γ-Bi_2O_3. Cationic deficiency in *M* tetrahedra leads to a remarkable electron deficiency of O(3) atoms. As a result, the valency forces of Bi atoms on the Bi—O(3) bonds are increased and these distances are reduced. The O(3) atom is located on the threefold axis and is a common vertex for the three Bi polyhedra which are symmetrical relative to it. The atoms are arranged in such a way that it is impossible to significantly reduce the Bi—O(3) distances by O(3)-atom shifts alone. Probably, in this case, reduction of Bi—O(3) bond lengths is mainly accounted for by Bi-atom shifts. At the same time the Bi—$O(1^{ii})$ bond length increases (Fig. 3*b*). Changes in the other 60% of Bi polyhedra of the γ-Bi_2O_3 structure are not so significant compared with the 40% of polyhedra considered above. However, these also contribute to the geometrical characteristics of an averaged Bi polyhedron within the structure. The above-mentioned redistribution of bond lengths in Bi polyhedra of γ-phase Bi_2O_3 is confirmed by comparison of the geometry of these polyhedra in the structures of $Bi_{12}GeO_{20}$ and γ-Bi_2O_3 (Table 3). For instance, in γ-Bi_2O_3 the Bi—$O(1^{iii})$ and Bi—O(3)



(*a*)

(*b*)

Fig. 3. (*a*) A projection of the structure of an ideal sillenite $Bi_{12}GeO_{20}$ on the (001) plane. (*b*) Bi-atom polyhedron in the structure of the ideal sillenite.

Table 3. *Interatomic distances* (Å) *in* Bi *polyhedra of* $Bi_{12}GeO_{20}$ *and* γ-Bi_2O_3

	$Bi_{12}GeO_{20}$	γ-Bi_2O_3
Bi—O(1^{i})	2.072 (1)	2.045 (3)
Bi—O(1^{ii})	2.221 (1)	2.402 (3)
Bi—O(1^{iii})	2.622 (1)	2.456 (3)
Bi—O(2)	2.2146 (6)	2.278 (3)
Bi—O(3^{iv})	2.6241 (8)	2.561 (3)

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) $1 - x, 1 - y, -1 + z$.

bond lengths are shorter by 0.17 and 0.06 Å, while the Bi—O(1^{ii}) and Bi—O(2) bond lengths are longer by 0.18 and 0.06 Å, respectively, as compared to similar bond lengths in $Bi_{12}GeO_{20}$.

A detailed comparison of the geometries of Bi polyhedra in the structures of $Bi_{12}GeO_{20}$ (Radaev, Muradyan, Simonov, Sarin *et al.*, 1990) and (Bi,Fe), (Bi,Zn) sillenites (Radaev, Muradyan & Simonov, 1990) which also exhibit O(3)-atom deficiency revealed changes in the Bi—O bond lengths in the latter, similar to the changes considered in this work: the Bi—O(3) bonds were shortened while the Bi—O(1^{ii}) bonds were lengthened as compared to similar ones in $Bi_{12}GeO_{20}$. This fact is indirect evidence of the above-suggested atomic model of γ-phase Bi_2O_3.

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Applications and Limitations of the Ionic Potential Model with Empirically Derived Ion-Specific Repulsion Parameters

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Abstract

A consistent set of ion-specific short-range repulsion parameters (*A* and *B*) has been assessed using the potential-energy minimization program *WMIN*. The values of the 'softness parameters' *B* were determined by quadratic extrapolation from isoelectronic species previously derived from vibrational data. The repulsion radii, *A*, were refined from known crystal structures minimizing their lattice energy while *B* was kept invariant. Repulsion radii and softness parameters show reasonable corre-

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