Chem. Mater. **2002,** *14,* 3471−3476

A Stoichiometric Model for Sillenites

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Received April 4, 2002. Revised Manuscript Received May 29, 2002

A critical review of crystallographic studies on sillenite compounds has allowed us to develop a general structural formula for the stoichiometric sillenites: $Bi_{12}(Bi_{4/5-nx}M^{n+}{}_{5x})O_{19.2+nx}$. We defined the stoichiometric sillenites as those with an oxygen sublattice that is fully occupied by either oxygen ions or lone electron pairs of Bi^{3+} ions. Nonstoichiometric groups of sillenites were identified as being either substoichiometric, with a deficient oxygen sublattice, or superstoichiometric, with an excess of oxygen. The compositions of the sillenites reported in the literature agree well with the proposed stoichiometric model. Two sillenites, Al and Zn, that were found to deviate from this model were experimentally investigated using X-ray diffraction, scanning electron microscopy, and wavelength-dispersive spectroscopy. The composition was found to be different from that reported previously and to correspond to the proposed stoichiometric model.

I. Introduction

Sillenite compounds display a variety of advantageous physical properties that make them very important technological materials. The current applications of sillenites are mainly in the fields of electrooptics, acoustics, and piezotechnics, where their physical properties such as photorefractivity, optical activity, photoconductivity, piezo-modulus, the velocity of ultrasound wave propagation,[1−3] etc., can be exploited. Recently, however, sillenites have begun to be considered for use as dielectrics in the field of electronics.[4] For the majority of these applications, the properties of the sillenites must be optimized or tuned to a certain value, and the adjustment of the properties to the requirements of a particular application demands a detailed understanding of the physics, the processing (crystal growth, film deposition, sintering, etc.), and the chemistry of the sillenites.

The parent representative of the sillenites is γ-Bi_2O_3, a metastable compound that can be prepared only by controlled cooling.[5] The crystal structure of γ-Bi_2O_3 has been the subject of a number of investigations that resulted in several different structural models.[6−8] All of the models have similar description of the structural framework that consists of the Bi−O coordination polyhedra. The Bi^{3+} ions within the framework are in octahedral coordination with the apical oxygen ion at a very short distance of ∼2.05 Å, with the two basal-plane oxygen ions at ∼2.2 Å, and with another two at ∼2.6 Å. The two oxygen ions from the adjacent octahedra are at a relatively long distance of ∼3.1 Å from Bi^{3+} and are not usually considered as being part of the first coordination sphere. Opposite the apical oxygen, a stereochemically active $6s^2$ lone electron pair that completes the distorted octahedra extends over a distance of ∼1.8 Å. The Bi−O octahedra share corners to form the framework, within which the regular tetrahedral sites are occupied by M-site Bi ions.

The structure and the occupancy of the M-site coordinational tetrahedra are the most disputed details of the γ-Bi_2O_3 crystal structure. Several authors have proposed several different solutions. Craig and Stephenson[6] assumed a statistically alternating occupancy of the tetrahedral position by the Bi^{3+} and Bi^{5+} ions, with a fully occupied oxygen sublattice. This structural formula, which was the most widely accepted structural model for a long time, should be written as $Bi_{12}(Bi^{3+}{}_{0.5}$-$Bi^{5+}{}_{0.5})O_{20}$. The model suffers from a major crystallographic inconsistency related to the dimensions of the ions: it is highly unlikely that the large Bi^{3+} ion with its stereochemically active $6s^2$ lone electron pair can fit into the tetrahedral interstice. Watanabe et al.[7] tried to avoid the tetrahedrally coordinated Bi^{3+} by proposing a model in which the tetrahedral sites are fully occupied by the Bi^{5+}. Because this model again assumes a fully occupied oxygen sublattice the charge compensation necessitates a deficiency in the Bi−O framework. The structural formula should be written as $Bi^{3+}{}_{11.67}Bi^{5+}O_{20}$. Unfortunately, a lack of experimental evidence for the presence of the Bi^{5+} ions has raised doubts about the validity of this model. In addition, the Bi^{5+} ion is destabilized at high temperatures and, therefore, not expected to exist in the high-temperature form of Bi_2O_3.

Today, many researchers (see, for example, refs 9−12) seem to agree that the structural model of Radaev and Simonov[8] describes the γ-Bi_2O_3 crystal structure in such a way that it can explain all of the experimental observations. According to this model, the tetrahedral positions are 80% occupied by Bi^{3+} ions and 20% vacant. The Bi^{3+} ions are coordinated with three oxygen ions,

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(1) Huignard, J. P.; Micheron, F. *Appl. Phys. Lett.* **1976**, *29*, 591.
(2) Hou, S. L.; Oliver, D. S. *Appl. Phys. Lett.* **1971**, *18*, 325.
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(5) Radaev, S. F.; Simonov, V. I.; Kargin, Y. K. *Acta Crystallogr. B* **1992**, *B48*, 604.
(6) Craig, D. C.; Stephenson, N. C. *J. Solid State Chem.* **1975**, *15*, 1.
(7) Watanabe, A.; Kodama, H.; Takenouchi, S. *J. Solid State Chem.* **1990**, *85*, 72.
(8) Radaev, S. F.; Simonov, V. I. *Sov. Phys. Crystallogr.* **1992**, *37*, 484.

10.1021/cm021173l CCC: $22.00

and in the direction of the absent fourth oxygen, the $6s^2$ lone electron pair extends (identified as the [BiO_3] group). The vacant tetrahedral positions are regularly coordinated with four oxygen ions (to give the [$\square O_4$] group, where $\square$ is a vacancy) and statistically distributed over the lattice. The model assumes that the oxygen vacancies are due only to the presence of the [BiO_3] groups, which is reflected in the structural formula $Bi_{12}(Bi^{3+}{}_{0.8}\square_{0.2})O_{19.2}$. It should be mentioned that the work of Murray et al.,[13] which preceded the study of Radaev and Simon[8] and was performed on the isomorphous compound $Bi_{12}PbO_{19}$, already suggested the presence of [MO_3] groups when the M ions exhibit a lone electron pair ([PbO_3] in the case of $Bi_{12}PbO_{19}$). In addition, for B^{3+} ions with a similar electronic configuration of the outer electron shell, the possibility of forming [BO_3] groups has been demonstrated as well.[14]

The possibility of stabilizing metastable γ-Bi_2O_3 using a small amount of other cations has already been suggested by Sillen.[15] Since then, numerous sillenites with very different stoichiometries have been reported. The cations that incorporate into the tetrahedral site have different valence states and sizes ranging from as small as B^{3+} to as large as an ionic radius of ~0.6−0.7 Å (e.g., Zn^{2+}, Cd^{2+}). Because of the wide variety of reported stoichiometries no stoichiometric model (or general structural formula) that would reflect the mechanism of isomorphous substitution corresponding to the structural facts and describing all of the sillenite compositions has yet been proposed. The goal of this paper is to contribute to the systematics of sillenites by developing a general formula for sillenites, and using this formula as a basis, experimentally investigate or critically review reported sillenite compositions.

II. Experimental Section

Aluminum and zinc sillenites were synthesized using solid-state reaction techniques. The corresponding mixtures of dried reagent-grade Bi_2O_3 (99.975%, Alfa Aesar), Al_2O_3 (99.99%, Alfa Aesar), and ZnO (>99.999% Alfa Aesar) were homogenized, repeatedly fired under subsolidus conditions (for zinc sillenite at ≤700 °C and for aluminum sillenite at ≤760 °C), and ground to enhance the reaction and reach equilibrium. The powders were then milled with Y-stabilized ZrO_2 milling balls to an average particle size of 1 μm, uniaxially pressed into pellets at approximately 150 MPa and sintered at 725 °C for the zinc sillenite and at 760 °C for the aluminum sillenite.

The progress of the reactions was monitored with a powder X-ray diffractometer (Philips PW1710) using the step−scan method and Cu Kα radiation; the step size was 0.04°, and the collection time was 2 s per point. The final product was examined with a high-resolution X-ray diffraction camera (Siemens D-5000) using a step size of 0.02° and a collection time of 60 s per point. Microstructural analyses of the ceramics were conducted using a scanning electron microscope (JEOL, JXA 840A) equipped with a wavelength-dispersive-spectroscopy (WDS) system for quantitative microanalyses.

III. Results and Discussion

A. Stoichiometric Model. Although the γ-Bi_2O_3 with the structural formula $Bi_{12}(Bi_{4/5}\square_{1/5})O_{19.2}$, is cation-deficient, substituents cannot be simply incorporated by filling the vacant cation sites. Such a direct incorporation of cations, which, because of a charge compensation must be associated with the incorporation of oxygen ions, would necessitate the formation of [BiO_4] groups. These groups, as mentioned earlier, are unlikely to exist. Consequently, although the oxygen sublattice is oxygen-deficient, it can be treated as virtually fully occupied. The reason for this is that the sites unoccupied by oxygen ions are filled by the $6s^2$ lone electron pairs of the Bi^{3+} ions. Such sillenites can be considered as stoichiometric sillenites. The incorporation of additional oxygen ions into the sublattice is possible only when the concentration of lone electron pairs is correspondingly reduced. This mechanism can be translated into a fundamental condition for the isomorphous substitution of sillenites: the incorporation of a cation must be associated with a corresponding decrease in the Bi concentration on the M-site of the sillenite crystal structure. The required decrease in the Bi concentration depends on the charge of the substitutents. A deviation from this rule requires a structural change in the Bi−O framework, and such sillenites can be considered as nonstoichiometric.

B. Sillenites with M^{2+} Ions. Following the fundamental structural condition for the isomorphous substitution of sillenites, the mechanism of the incorporation of M^{2+} ions can be derived. The M^{2+} ions occupy the tetrahedral site in such a way that three of the ions enter the vacant site while two of the ions substitute for the Bi^{3+} ions. The removal of the Bi^{3+} ions, together with their lone electron pairs, from the tetrahedral site opens the space in the oxygen sublattice for the incorporation of two oxygen ions, as required for charge compensation. The substitution can be described by the structural formula

$$Bi_{12}(Bi_{4/5-2x}M^{2+}{}_{5x}\square_{1/5-3x})O_{19.2+2x} \qquad (1)$$

It is obvious that such a substitution mechanism must have an upper limit for the M^{2+} incorporation (x_{max}): when all of the vacant tetrahedral sites are occupied ($^1/_5 - 3x = 0$) no additional M^{2+} can be incorporated. The structural formula for the sillenites saturated with M^{2+} ions can be calculated from formula 1 by taking $x_{max} = {}^1/_{15}$. We then obtain

$$Bi_{12}(Bi_{2/3}M^{2+}{}_{1/3})O_{19.33} \qquad (2)$$

Because the parent γ-Bi_2O_3 is a metastable phase, the structural formula 1 cannot imply a thermodynamic stability range for such sillenites. At a certain concentration, the incorporation of the cations into γ-Bi_2O_3 does result in the stabilization of the sillenite phase. However, this phase is not necessarily stable at room temperature and might be stable only at elevated temperatures. Usually, the most stable phases are the end members which is the reason they are the most intensively investigated.

The most comprehensively investigated in the series of M^{2+} sillenites are the cadmium, cobalt, and zinc

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(9) Vannier, R. N.; Abraham, F.; Nowogrocki, G.; Mairesse, G. *J. Solid State Chem*. **1999**, *142*, 294.

(10) Champarnaud-Mesjard, J. C.; Frit, B. *C. R. Acad. Sci. II C*, **1999**, *2*, 369.

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(13) Murray, A. D.; Catlow, C. R. A.; Beech, F.; Drennan, J. *J. Solid State Chem*. **1986**, *62*, 290.

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(15) Sillen, L. G. *Arkiv Kemi* **1937**, *12A*, 1.

sillenites. The stoichiometry of cadmium sillenite reported in the powder diffraction file (PDF)[16], card #41-0135, perfectly matches the proposed formula. Later, this was confirmed by the work of Champarnaud-Mesjard et al.[10] On the basis of a Rietveld analysis of X-ray diffraction patterns of samples with $x = 0.0667$, 0.0322, and 0.0064, they proposed a mechanism of Cd incorporation into γ-Bi_2O_3 similar to the proposed by formula 1. The structural analysis of cobalt sillenite performed by Mary et al.[11] also confirmed the presence of $[BiO_3]$ groups and revealed a stoichiometry of $Bi_{12.7}Co_{0.3}O_{19.35}$, which is again close to the proposed model. Zinc sillenites have been studied by many authors. Craig and Stephenson[6] determined the composition with a cation ratio that corresponds to x_{max}. However, they claim the presence of Bi^{5+} ions in the tetrahedral site and a fully occupied oxygen sublattice. This study was corrected by Radaev and Simonov,[8] who determined a stoichiometry of $Bi_{12}(Bi_{0.67}Zn_{0.33})O_{19.33}$, which perfectly matches the structural formula proposed in this paper.

In addition to the structures described in these three studies, a number of other compositions with M^{2+} have been proposed by several authors. As a rule, these studies are not documented well, or they introduce unsound and/or improbable crystallographic solutions. In particular, the studies of Ramanan et al.[17] and Kirik et al.[18] were subjected to strong criticism in the literature (e.g., refs 7 and 8). They proposed sillenite compositions such as $Bi_{18}Ni_8O_{36}$, $Bi_{12}NiO_{19}$, $Bi_{18}Mg_8O_{36}$, $Bi_{12}MgO_{19}$, etc., and $Bi_{12}ZnO_{20}$, $Bi_{10}Cd_3O_{18}$, etc., respectively. The same two groups have also published other papers with similarly questionable crystallographic solutions and proposed compositions such as $Bi_{12}CdO_{19}$, $(Bi_{19.68}Ni_{4.32})Ni_2O_{40}$, etc.[19,20]

The X-ray photoelectron spectroscopy and optical studies of the Zn-analogue performed by Zaldo et al.[21] confirmed the presence of $[BiO_3]$ groups; however, using X-ray photoemission spectroscopy, they determined the composition of a single crystal to be $Bi_{12}Zn_{0.57}Bi_{0.43}O_{19.2}$ and proposed the mechanism of substitution to be $Bi_{12}(Zn_yBi_{1-y})O_{20-\delta}$. Certainly, such a mechanism is highly unlikely for $y < {}^1/_3$, whereas for $y > {}^1/_3$, it necessitates the formation of a new type of oxygen vacancy in addition to those associated with the $[BiO_3]$ groups. Unfortunately, they did not comment on this issue, nor on the fact that the same single-crystal growth method (Czochralski method) applied by Radaev and Simonov[8] resulted in a significantly different stoichiometry.

Because of repeated reports of zinc sillenites with a Zn occupancy of the M site higher than 0.33 (see also, refs 22−24), which is in contradiction with the model proposed, we investigated this possibility in detail. The nominal composition $6Bi_2O_3$:ZnO, which corresponds to the hypothetical $Bi_{12}ZnO_{20}$, was repeatedly fired to reach equilibrium. The routine X-ray diffraction pattern shows only the peaks of sillenite phase, which might misleadingly suggest the successful synthesis of $Bi_{12}ZnO_{20}$ (Figure 1). A microstructural analysis of the sintered powder revealed the presence of a small amount of ZnO phase within the Bi-rich matrix (Figure 2). The Bi-rich matrix was analyzed by WDS, and the results obtained can be written as $Bi_{12.67(8)}Zn_{0.34(2)}O_{19.33}$, which corresponds to the Bi-to-Zn ratio determined by Craig and Stephenson[6] and Radaev and Simonov.[8] According to the WDS analysis, we calculated that only 3 vol % of the ZnO is to be expected in the mixture, which, together with the fact that the X-ray scattering factor for ZnO is much smaller than that for a Bi-rich sillenite phase, explains the problems of detecting the ZnO phase in the X-ray diffraction patterns. Consequently, we performed a detailed scan over the 2θ range where the most intense ZnO peaks are expected and detected their presence (Figure 1).

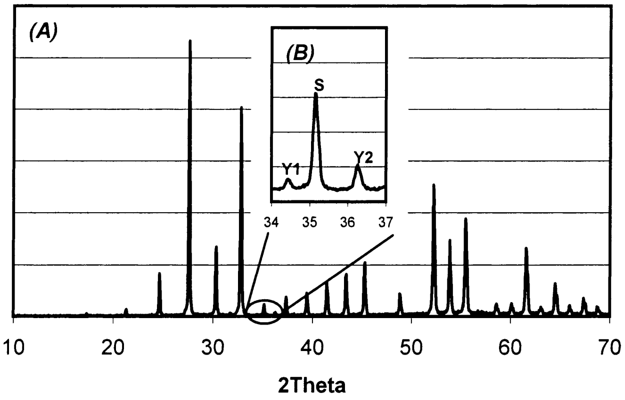

Figure 1. X-ray diffraction pattern of the powder with nominal composition $6Bi_2O_3$:ZnO fired repeatedly at 700 °C. All diffraction lines in pattern A correspond to the sillenite structure, while the lines of ZnO are seen in high-resolution pattern B. The diffraction line S is the [400] line of the sillenite with $I/I_o = 3$, while Y1 and Y2 are the [002] and [101] lines of ZnO with $I/I_o = 42$ and 100, respectively.

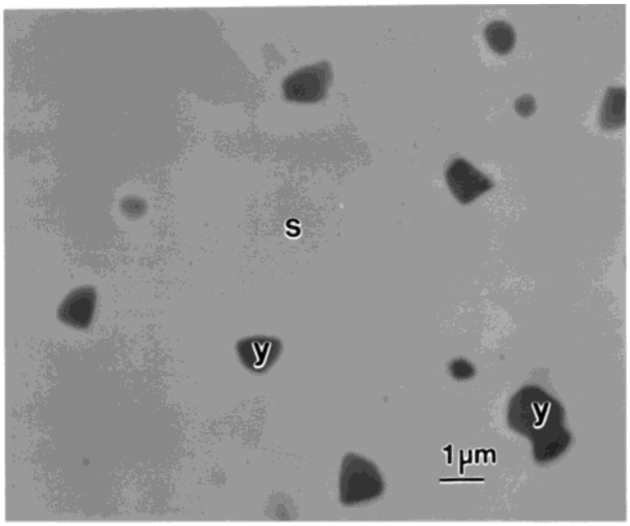

Figure 2. Backscattered electron microscope image of ceramics with the nominal composition $6Bi_2O_3$:ZnO sintered at 700 °C (s = sillenite phase, y = ZnO)

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[16] *Powder Diffraction File*, International Centre for Diffraction Data: Newtown Square, PA, 2001.

[17] Ramanan; A.; Gopalakrishnan, J.; Rao, C. N. R. *Mater. Res. Bull.* **1981**, *16*, 169.

[18] Kirik, S. D.; Kutvinskii, V. A.; Koryagina T. I. *J. Struct. Chem.* **1985**, *24*, 569.

[19] Rangavittal, N.; Guru Row, T. N.; Rao, C. N. R. *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 409.

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[22] Betsch, R. J.; White, W. B. *Spectrochim. Acta* **1978**, *34A*, 505.

[23] Kargin, Y. F.; Marin, A. A.; Skorikov, V. M. *Inorg. Mater.* **1982**, *18*, 1375.

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From this experiment, we can conclude that even if there is an excess of Zn in the starting mixture, the concentration of Zn in the sillenite synthesized with a solid-state reaction will be no higher than that expected by the structural formula 2. However, this study cannot answer the question as to whether other preparation methods (e.g., single-crystal growth with the Czochralski method) under specific conditions might result in the formation of nonstoichiometric zinc sillenites such as those reported by Zaldo et al.[21]

C. Sillenites with M^{3+} Ions. M^{3+} ions incorporate into γ-Bi_2O_3 following the same mechanism as M^{2+}. The difference is only in the concentration of substituted Bi^{3+} ions. For two M^{3+} ions occupying the vacant tetrahedral sites, three M^{3+} ions substitute for the Bi^{3+} in the $[BiO_3]$ groups and allow the incorporation of three oxygen ions to compensate the charge. This can be written using the structural formula

$$Bi_{12}(Bi_{4/5-3x}M^{3+}_{5x}\square_{1/5-2x})O_{19.2+3x} \qquad (3)$$

The upper limit for the M^{2+} incorporation occurs when all of the vacant tetrahedral sites are occupied ($x_{max} = {}^1/_{10}$). The structural formula for the sillenites saturated with M^{3+} ions can be written as

$$Bi_{12}(Bi_{1/2}M^{3+}_{1/2})O_{19.5} \qquad (4)$$

As in the case of M^{2+} sillenites, the stoichoimetry of the comprehensively investigated M^{3+} sillenites also matches the structural formulas 3 and 4. The $Bi_{12}(Bi_{1/2}M^{3+}_{1/2})O_{19.5}$ composition is reported for $M^{3+} = Ga^{3+}$, Fe^{3+}, Cr^{3+} and Tl^{3+}.[8,25,26] Earlier works on gallium and iron sillenites[6,27] proposed the same cation ratio while mistakenly assuming the presence of Bi^{5+}. If we do not consider the studies that were later disproved, such as ref 19, there are only a few reports about compositions that deviate from formula 4. Analogous to the zinc sillenites, Zaldo et al.[21] reports the same substitution mechanism for the gallium sillenites, i.e., $Bi_{12}(Ga_yBi_{1-y})O_{20-\delta}$, but they do not comment on the structural consequences of such a mechanism. Yudin et al.[28] report the composition of $Bi_{12}GaO_{20}$, however, their crystallographic analysis suffers from high discrepancy indices. Romanov et al.[29] claimed the existence of a metastable indium sillenite with the composition $Bi_{24}(Bi^{5+}_{0.96}In_{1.04})O_{39.97}$, which, in terms of the cation ratio, again closely corresponds to formula 4.

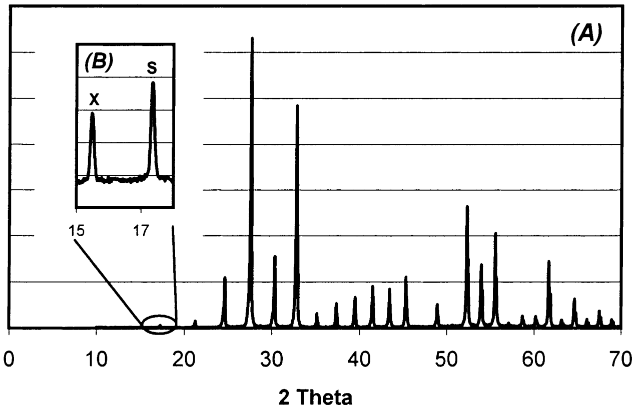

Figure 3. X-ray diffraction pattern of the powder with nominal composition $12Bi_2O_3$:Al_2O_3 fired repeatedly at 760 °C. All diffraction lines in pattern A correspond to the sillenite structure, while the lines of $Al_4Bi_2O_9$ are seen in high-resolution pattern B. The diffraction line S is the [200] line of the sillenite with $I/I_o = 1$ and the diffraction line X is the [001] line of $Al_4Bi_2O_9$ with $I/I_o = 100$.

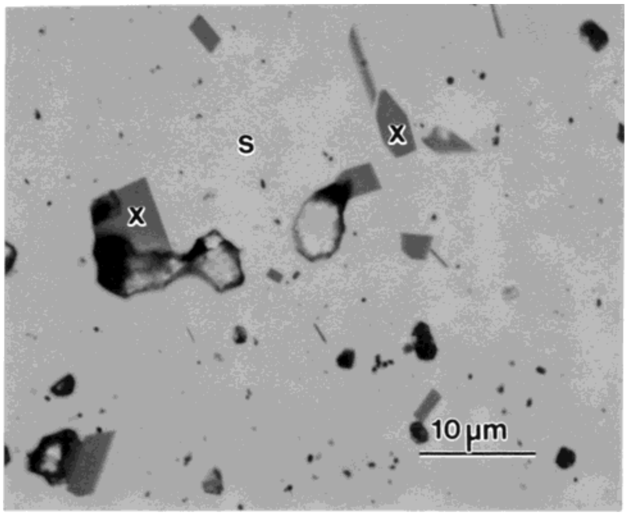

Figure 4. Backscattered electron microscope image of ceramics with the nominal composition $12Bi_2O_3$:Al_2O_3 sintered at 760 °C (s = sillenite phase, x = $Al_4Bi_2O_9$ inclusion).

PDF cards #42-0180 and #42-0184 based on the work of Levin and Roth[30] report the stoichiometries of $Bi_{24}Ga_2O_{39}$ and $Bi_{24}Al_2O_{39}$. To reexamine these results, and because the composition of aluminum sillenite has not yet been a subject of comprehensive investigation, we synthesized the nominal composition $12Bi_2O_3$:Al_2O_3, which corresponds to the hypothetical $Bi_{24}Al_2O_{39}$. As for the Zn-analogue, the routine X-ray diffraction pattern again shows only the peaks of the sillenite phase. The detailed X-ray diffraction analysis of range $15° < 2\theta < 18°$ reveals the [001] diffraction line of $Al_4Bi_2O_9$ (Figure 3). The SEM analysis of a sintered sample confirms the presence of a small amount of secondary Al-rich phase (Figure 4). The WDS microanalysis of the matrix sillenite phase revealed a composition of $Bi_{12.47(7)}Al_{0.53(4)}O_{19.5}$, which, within the analytical error, corresponds to the structural formula 4. This raises doubts about the stoichiometries reported in the PDF cards. Although the nominal composition contained an excess of Al_2O_3, the determined concentration of Al in the aluminum sillenite synthesized by a solid-state-reaction method was no higher than that described by x_{max}.

D. Sillenites with M^{4+} Ions. Five M^{4+} ions incorporate into γ-Bi_2O_3 in such a way that one fills the vacant tetrahedral site while four substitute the tetrahedrally coordinated Bi^{3+} ion. This opens space for the incorporation of four oxygen ions to compensate for the charge. The mechanism can be written

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(25) Radaev, S. F.; Muradyan, L. A.; Kargin, Y. F.; Volkov, V. V.; Sarin, V. A.; Rider, E. E.; Simonov, V. I. *Kristallografiya* **1990**, *35*, 1126.

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$$\mathrm{Bi}_{12}(\mathrm{Bi}_{4/5-4x}\mathrm{M}^{4+}{}_{5x}\square_{1/5-x})\mathrm{O}_{19.2+4x} \qquad (5)$$

The upper limit for such a mechanism of incorporation occurs at $x_{\max} = {}^{1}/_{5}$ and results in sillenites with no Bi^{3+} ions in the tetrahedral site and a formula of

$$\mathrm{Bi}_{12}\mathrm{M}^{4+}\mathrm{O}_{20} \qquad (6)$$

Many M^{4+} sillenites have been synthesized so far also because the tetrehedral sites can be occupied by a combination of ions that gives a total charge of 4+ (e.g., $\mathrm{M}^{4+} = {}^{1}/_{2}\mathrm{M}^{3+} + {}^{1}/_{2}\mathrm{M}^{5+} = {}^{1}/_{3}\mathrm{M}^{2+} + {}^{2}/_{3}\mathrm{M}^{5+}$). With respect to the stoichiometry of M^{4+} sillenites, not much disagreement is present in the literature. Several M^{4+} analogues with comprehensively studied compositions include $\mathrm{Bi}_{12}\mathrm{SiO}_{20}$,[31] $\mathrm{Bi}_{12}\mathrm{TiO}_{20}$,[32,33] $\mathrm{Bi}_{12}\mathrm{GeO}_{20}$,[8] $\mathrm{Bi}_{12}\mathrm{MnO}_{20}$,[34] and $\mathrm{Bi}_{12}(\mathrm{B}_{0.5}\mathrm{P}_{0.5})\mathrm{O}_{20}$.[35] Even M^{4+} sillenites with vacancies at the tetrahedral site can be, according to the model proposed, considered as stoichiometric as long as the oxygen sublattice is fully occupied. An example of such a sillenite is $\mathrm{Bi}_{12}(\mathrm{Fe}_{0.35}\mathrm{P}_{0.59}\square_{0.06})\mathrm{O}_{20}$.[8]

In addition to stoichiometric M^{4+} sillenites, a few examples of nonstoichiometric sillenites have been reported and are well-documented. These are single crystals with the compositions $\mathrm{Bi}_{12}\mathrm{Ti}_{0.90}\mathrm{O}_{19.80}$,[8] $\mathrm{Bi}_{12}\mathrm{Ge}_{0.87}\mathrm{O}_{20-\delta}$, and $\mathrm{Bi}_{12}\mathrm{Si}_{0.87}\mathrm{O}_{20-\delta}$,[36] all grown by the Czochralski method.

E. Sillenites with M^{5+} Ions. The difference in the charge between an M^{5+} substituent ion and a Bi^{3+} ion can be compensated by the incorporation of one additional oxygen ion. Therefore, each B^{3+} ion directly substitutes for one M^{5+} ion and one oxygen ion that fills the space previously occupied by the Bi^{3+} lone electron pair. The structural formula can be written as

$$\mathrm{Bi}_{12}(\mathrm{Bi}_{4/5-x}\mathrm{M}^{5+}{}_{x}\square_{1/5})\mathrm{O}_{19.2+x} \qquad (7)$$

Such a mechanism requires constant concentration of the tetrahedral vacancies, which tells us that the upper limit of this homogeneity range will be limited not by the vacancy concentration, as with other types of the sillenites, but by the concentration of the tetrahedral Bi^{3+} ions. The upper limit occurs when all of the Bi^{3+} ions are removed from the tetrahedral sites, which gives $x_{\max} = {}^{4}/_{5}$ and the structural formula

$$\mathrm{Bi}_{12}(\mathrm{M}^{5+}{}_{4/5}\square_{1/5})\mathrm{O}_{20} \qquad (8)$$

Only three representatives of the M^{5+} sillenites are reported in the literature: V^{5+}, As^{5+}, and P^{5+}. In addition, the existence of a niobium sillenite phase with 2.36 mol % of $\mathrm{Nb}_2\mathrm{O}_5$[37] was also reported to be stable at room temperature. In contrast, the niobium sillenite was considered as a metastable phase by Levin and Roth[30] and was not included in their $\mathrm{Bi}_2\mathrm{O}_3{-}\mathrm{Nb}_2\mathrm{O}_5$ phase diagram.[38] No further information that would indicate the stoichiometry of the Nb sillenite was reported.

The crystal chemistry of M^{5+} sillenites differs from other analogues because the highly charged M^{5+} ions induce structural changes within the Bi−O framework. These changes allow for the accommodation of additional oxygen ions and the formation of superstoichiometric sillenite compositions.[8] The distortion of the framework might also provide the possibility of incorporating some Bi^{5+} ions as suggested by Hardcastle et al.[39] The investigations of vanadium sillenites performed by Soubeyroux et al.[40] were focused on the entire homogeneity range, and they proposed the general formula $\mathrm{Bi}_{12}(\mathrm{Bi}_x\mathrm{V}_{4/5-x}\square_{1/5})\mathrm{O}_{20}$. Although they assumed all of the Bi at tetrahedral positions to be Bi^{5+}, they proposed the same variation of the cation ratio along the homogeneity range as in formula 7. They claimed the end member of this homogeneity range to be $\mathrm{Bi}_{12}(\mathrm{V}_{4/5}\square_{1/5})\mathrm{O}_{20}$. In analogy to to vanadium sillenites, they also proposed the same stoichiometry for the arsenic and phosphorous sillenite end members.[41] The studies were taken forward by Watanabe et al.[7,42] and Radaev and Simonov,[8] who discovered a range of superstoichiometric compositions that extend for P to 7.15 mol %, for As to 6.74 mol %, and for V to 6.88 mol %. The structural mechanism of the formation of superstoichiometric sillenites was investigated by Radeav and Simonov.[8] They performed their studies on a vanadium sillenites single crystal grown by the Czochralski method, disproved the existence of Bi^{5+}, and proposed a structural formula of $\mathrm{Bi}_{12}(\mathrm{Bi}^{3+}{}_{0.03}\mathrm{V}_{0.89}\square_{0.08})\mathrm{O}_{20.27}$.

F. General Considerations. The structural formulas for the individual types of sillenites (formulas 1, 3, 5, and 7) can be generalized, and a single formula for all of the stoichiometric sillenites can be written as

$$\mathrm{Bi}_{12}(\mathrm{Bi}_{4/5-nx}\mathrm{M}^{n+}{}_{5x}\square_{1/5-(5-n)x})\mathrm{O}_{19.2+nx} \qquad (9)$$

or more simply

$$\mathrm{Bi}_{12}(\mathrm{Bi}_{4/5-nx}\mathrm{M}^{n+}{}_{5x})\mathrm{O}_{19.2+nx} \qquad (10)$$

where n is the charge on the M ion. Formula 9 can also be applied to hypothetical M^{+} and M^{6+} sillenites; however, there are no properly documented reports in the literature on the existence of such types of sillenites. The reason the M^{+} sillenites are not stable might be the large ionic size of the M^{+} ions. The incorporation of stoichiometric M^{6+} sillenites necessitates an increase in the concentration of tetrahedral vacancies according to the formula $\mathrm{Bi}_{12}(\mathrm{Bi}_{4/5-6x}\mathrm{M}^{6+}{}_{5x}\square_{1/5+x})\mathrm{O}_{19.2+6x}$. Such a mechanism, combined with the fact that the large charge of the M^{6+} ions necessarily causes distortions in the Bi−O framework (which was already shown for the

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M^{5+} sillenites), might be unfavorable for the stability of the compound.

Judging from the structure of the oxygen sublattice, two types of nonstoichiometric sillenites were identified in addition to the stoichiometric sillenites that exhibit an oxygen sublattice that is fully occupied with either oxygen ions or lone electron pairs. Substoichiometric sillenites exhibit vacancies in the oxygen sublattice, while the superstoichiometric sillenites exhibit an excess of oxygen ions. A superstoichiometry appears only for M^{5+} sillenites, which was attributed to the highly charged tetrahedral M^{5+} ions that induce distortions of the Bi−O framework. The representatives of the substoichiometric sillenites are $Bi_{12}Zn_{0.57}Bi_{0.43}O_{19.2}$, $Bi_{12}Ga_{0.63}Bi_{0.37}O_{19.2}$, $Bi_{12}Ga_{0.72}Bi_{0.28}O_{19.5}$,[21] $Bi_{12}Ti_{0.90}O_{19.80}$,[8] $Bi_{12}Ge_{0.87}O_{20-\delta}$, and $Bi_{12}Si_{0.87}O_{20-\delta}$.[36] Interestingly, all of these compositions were determined on single crystals grown by the Czochralski method. Santos et al.[43] investigated the compositional variations along the cross sections of the single crystals grown by the Czochralski method. They revealed that the core formation, which appears on such single crystals and has already been reported by several authors (e.g., refs 44 and 45) is related to the deficiency of M ions and necessarily results in a certain degree of nonstoichiometry. The degree of nonstoichiometry is variable for a particular sillenite and is related to the parameters of the crystal growth.

IV. Summary

On the basis of the crystallographic facts and the mechanisms of isomorphic substitution, a general formula for the stoichiometric sillenites, $Bi_{12}(Bi_{4/5-nx}M^{n+}{}_{5x})O_{19.2+nx}$, was developed. The general formula describes the possible homogeneity range and its dependence on the charge of the tetrahedral M^{n+} ions; however, it does not prejudge the thermodynamic stability within this range. The literature review revealed good agreement for all of the comprehensively investigated stoichiometric sillenites with the stoichiometric model proposed. Two sillenites that, according to the literature data, deviate from the general formula were experimentally investigated. For zinc sillenite, the composition was determined to be $Bi_{12.67(8)}Zn_{0.34(2)}O_{19.33}$, and for aluminum sillenite, it was $Bi_{12.47(7)}Al_{0.53(4)}O_{19.5}$, which, in both cases, corresponds to the general formula. Apart from the stoichiometric sillenites, which were defined in this work as those with their oxygen sublattice fully occupied either by the oxygen ions or by the lone electron pairs of the Bi^{3+} ions, two nonstoichiometric groups of sillenites were identified: substoichiometric sillenites with a deficient oxygen sublattice and superstoichiometric sillenites with an excess of oxygen.

Acknowledgment. The authors acknowledge Mr. Borut Ambroželi for his valuable assistance during the experimental work.

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